CHAPTER ONE: INTRODUCTION

1.1 Background of the Study

The need for economical, sustainable, safe, and secure shelter is an inherent global problem, and numerous challenges remain in order to produce environmentally friendly construction products which are structurally safe and durable (Kandachar & Brouwer, 2002). The consumption of building components made of fibre reinforced cement is increasing rapidly especially in developed countries, and it ~~which~~ is estimated to be around several million ~~of~~ tonnes per year (Berhane, 1999). This is because with this type of material it is possible to produce lightweight building components, with good mechanical performance (mainly impact energy absorption) and suitable thermal-acoustic insulation and it is also economically feasible.

In developing countries, where the lack of housing as well as the lack of commercial, industrial and public service buildings is ~~considerable~~considerably high, the introduction of these materials can help in increasing the production of buildings with suitable performance. Provided that the low durability risks in alkaline environment are eliminated, the vegetable fibres can be a good alternative in these countries due to low cost. Besides, in some regions, asbestos–cement is still the sole composite in use, ~~although health hazards are becoming an increasing concern~~ but their health hazards are of increasing concern (Berhane, 1999).

From centuries, mankind has used the natural fibres for various types of application including building materials. In most ~~of the~~ countries, users have explored the possibilities of using the natural fibres from different plants, which include~~s~~ bagasse, cereal straw, corn stalk, cotton stalk, kenaf, rice husk/rice straw etc (Eze-Uzomaka & Nwadiuto, 1990). Most of the fibres were used mainly for the production of hard board and particle board. Emergence of mortar in the beginning of the ~~19th~~ 19th century has provided the researcher ~~the~~ with new dimensions to use the natural fibre in more diversified fields (Eze-Uzomaka & Nwadiuto, 1990). At the same time the necessity has also increased the interest in synthetic fibre like glass fibre which, due to its superior dimensional and other properties, seems to be gaining popularity and slowly replacing the natural fibre in different applications. As a result of this change in the raw material and production process of synthetic fibre based composites, energy consumption has increased (Fageiri, 1983). The environmental loss suffered by ~~the~~ society due to the pollution generation during the production and recycling of these synthetic based materials has once again drawn the attention ~~for~~ to the use of natural fibre. The renewed interest has resulted in the new ways of natural fibre modifications/use and brought

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it to be at par/superior to synthetic fibres. Now it is in use from making rope to spacecraft applications, and the building industry has also come out as one of its main beneficiaries (Saxena et al., 2008).

Natural fibers are prospective reinforcing materials and their use until now has been more traditional than technical. They have long served many useful purposes, but the application of materials technology for the utilization of natural fibers as reinforcement in cement has only taken place in comparatively recent years. The distinctive properties of natural fiber reinforced cement are of improved tensile and bending strength, greater ductility, and greater resistance to cracking and hence improved impact strength and toughness. Besides, its ability to sustain loads, natural fiber reinforced cement mortar is also required to be durable. Durability of vegetable fiber reinforced cement mortar is related to the ability to resist both external (temperature and humidity variations, sulfate or chloride attack etc) and internal damage (compatibility between fibers and cement matrix, volumetric changes etc). The degradation of natural fibers immersed in Portland cement is due to the high alkaline environment which dissolves the lignin and hemi cellulose phases thus weakening the fiber structure (Saxena et al., 2008).

Increasing concern about the global warming, primarily due to deforestation, has led to the ban on use of wood in government buildings in some countries. Subsequently, a large action plan for the development of wood substitute has resulted in the creation of more awareness about the use of natural fibre-based building materials. In the past one decade the joint efforts by R & D organizations, private industries and funding agencies provided the much needed thrust for the actual transfer of technical know-how and product to the end users.

Most of the developing countries are very rich in agricultural waste and natural fibre. Except a few exceptions, a large part of agricultural waste is being used as ~~a~~ fuel. Nigeria alone produces more than 400 million tonnes of agricultural wastes annually (Akpabio et al., 2012). It has got a very large percentage of the total world production of rice husk, jute, stalk, baggase and maize fibres. All these natural fibres can be utilized more effectively in the development of composite materials for various building applications.

1.2 Statement of Research Problem

There are large numbers of raffia palm trees growing in the tropical regions of the world and very abundant in southern Nigeria, where they are tapped for palm wine. The leaves, after the trees are tapped constitute waste which can be utilized for production of new construction materials. Not much work has been reported on the use of raffia palm fibers in cement. In the present research, experimental study will be carried out to investigate the strength and durability properties of raffia palm fibers on polymer modified cement mortar.

Vegetable fiber cement composites produced with ordinary Portland cement matrices undergo an aging process in humid environments in which they may suffer a reduction in post- cracking strength and toughness. This durability problem is associated with an increase in fiber fracture and decrease in fiber pull-out due to fiber mineralization (Ohama, 2006). This mineralization process is a result of migration of hydration products (mainly $Ca(OH)_2$) to the fiber structure. Efforts to develop durable cement composite laminates reinforced by long sisal fibers for structural purposes ~~has~~ have shown much promise recently (Ohama, 2006). A newly developed matrix with a low calcium hydroxide content was used. The use of natural fibre mortar-composites was already considered for concrete roofing in several parts of the world. However, the sensitivity of this fibre to the alkaline environment of the Portland cement matrix limits~~ed~~ ~~it´s~~ its application. In addition, the hydrophilic nature of this fibre associated with the rheological characteristics of the used matrices ~~limited~~ limits the fibre volume percent, the difficulty in material mixing and casting without increasing the water content in the mixtures.

The main drawback to the use of vegetable fibres is the durability of these fibres in a cementitious matrix and also the compatibility between both phases. The alkaline media weaken most natural fibres, especially the vegetable ones which are actually strands of individual filaments liable to be separated from each other. The mineralisation phenomenon can be associated with loss of composite tenacity in the long term. The severe degradation of exposed composites can also be attributed to interfacial damage~~s~~ due to continuous volume changes of the porous vegetable fibres ~~inside~~ in the cement matrix (Priya & Paul, 2002).

Amongst the several vegetable fibres available in the country, rafia palm fibre is of particular importance. This fibre is obtained from a rafia palm plant tropical regions of Africa, ~~and~~ especially Madagascar, with one species (*R. taedigera*) also occurring in Central and South America. They grow up to 16 m (52.5 ft) tall and are remarkable for their compound pinnateleaves, the longest in the plant kingdom; leaves of *R. regalis* up to 25 m (82.38 ft) long and 3 m (9.84 ft) wide (Akpabio et al., 2012).

1.3 Aim and Objectives of the Research

The aim of this research work is to prepare and evaluate the properties of raffia ralm fibre polymer modified cement (PMC) composites that could possibly yield low-cost indigenous construction materials (roofing sheets).

The objectives of this work are to:

i. characterize the raffia palm (fibre and particulate).
ii. produce raffia palm (fibre and particulate) polyester modified and polyvinyl alcohol modified cement mortars.
iii. characterize the polyester modified and polyvinyl alcohol modified cement mortar composites.
iv. study the varieties of the thermal analysis of the fibres and the composites
v. produce sample roofing sheets based on the research findings.

1.4 Significance of Study

i. This work is expected to develop a new class of cement mortar composite with improved mechanical, water absorption and thermal resistance using rafia palm fibre polymer modified cement (PMC) composites
ii. This research will add economic value to the abundant rafia palm fibre in Nigeria for the production of cement mortar composites for roofing sheets applications and reduce the environmental effect as a result of open burning which might led to CO_2 emissions.
iii. The research will also bring foreign exchange earnings for the country~~,~~ by exporting the Rafia Palm Fibre for production of high standard composites for roofing sheet application.

The results obtained in this research can act as a starting point for both industrial designers and researchers to design and develop cement mortar composites using agro-waste (raffia palm fibre) for roofing sheet applications that will be a great benefit to Nigeria and the world at large.

Furthermore, the following are the justification for carrying out this research.

i. Economic: Cement mortar composites made from rafia palm fibre are expected to be cheaper since the material is available in large quantity as waste in the country.

ii. The establishment of rafia palm fibre polymer modified cement (PMC) composite factories will create jobs and reduce unemployment.

iii. The use of rafia palm fibre for cement mortar composite manufacture will significantly reduce the green house gases emitted as a result of the disposal of rafia palm fibre to land fill

iv. The research will bring foreign exchange earnings for the country, by exporting the rafia palm fibre for production of high standard roofing sheets composites.

1.5 Scope of Study

The scope of this study includes;

(1) The sourcing and conditioning the raffia palm fibre stnadards

(2) The preparation of the raffia palm fibre ash particles.

(3) The characterization of the raffia palm (fibre and particulate)

(4) The determination of thermal properties of the raffia palm (fibre and particulate)

(5) Determining the effects of saline treatment on the fibre using factorization design, thus develop a model for predicting the tensile strength of the fibres within the selected experinmental conditions.

(6) Production of raffia palm (fibre and particulate) and polymer modified cement mortar composite.

(7) Determination the effects of curing time on the produced composite.

(8) Characterization of the polymer modified composite

(9) The development of a model that can be used in predicting the water absorbption and compressive strength of the polymer modified composite within the selected experimental condtions.

CHAPTER TWO: LITERATURE REVIEW

2.1 Historical Background of Composite Materials

Composites are an important class of engineering materials that are finding increasing use in applications ranging from leisure goods to construction; their excellent specific properties make them particularly attractive for applications in which weight saving is advantageous, such as transportation and aerospace (Mohanty et al., 2002). In composite materials, the idea of using cellulous fillers as reinforcement is neither new nor a recent one. Man had used this idea for a long time, since the beginning of our civilization when straw and grass were used to reinforce mud to make bricks.

Composite materials are engineering materials made up of two or more constituent materials (mixed and bonded) with different physical or chemical properties which remain separate and also distinct on a macroscopic scale within the finished structure (Aigbodion & Hassan, 2010).

Generally speaking, a composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is realized. According to the principle of combined action, better property combination is fashioned by the judicious combination of two, or more distinct materials (Callister, 1997).

2.2 Components of a Composite Material

In its most basic form, a composite material is one which is composed of at least two elements working together to produce material properties that are different from the properties of those elements on their own (Pamela, 2007). Most composites consist of a bulk material (the matrix), and reinforcement added primarily to increase the properties of the matrix.

2.2.1 Role of Matrix in a Composite

Many materials when they are in a fibrous form exhibit very good strength property, but to achieve these properties the reinforcement should be bonded by a suitable matrix. The matrix isolates the fibers from one another in order to prevent abrasion and formation of new surface flaws and acts as a bridge to hold the reinforcement in place. A good matrix should possess ability to deform easily under applied load, transfer the load onto the reinforcement and evenly distributive stress concentration (Pamela, 2007).

i. It binds the reinforcement together and acts as the medium by which an externally applied stress is transmitted and distributed to the reinforcement.
ii. Secondly, it protects the individual reinforcement from surface damage as a result of mechanical abrasion or chemical reactions with the environment.
iii. Finally, the matrix separates the fibers/particles and, by virtue of its relative softness and plasticity, prevents the propagation of brittle cracks from fiber to fiber which could result in catastrophic failure; hence it serves as a barrier to (crack) propagation.

2.2.2 Role of Reinforcement in a Composite

The reinforcement, in its basic form, is embedded in the bulk material (matrix), principally to give and improve the mechanical property of the matrix and the composite material at large (Pamela, 2007). The matrix which is continuous surrounds the other phase often called the dispersed phase, or, in our case, fibers. The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the reinforcement (dispersed phase). “Dispersed phase geometry” in this context means the shape of the fibers/particles and the particle size, distribution and orientation.

One simple scheme for the classification of composite materials is shown in Figure 2.1, which consists of three main divisions – particle reinforced, fiber reinforced, and structural composites. Also, at least two subdivisions exist for each. The dispersed phase for particle -reinforced composites is equiaxed (i.e. particle dimensions are approximately the same in all directions); for fiber reinforced composites, the dispersed phase has the geometry of a fiber (i.e., a large length – to – diameter ratio). Structural composites are combinations of composites and homogenous materials (Callister, 1997).

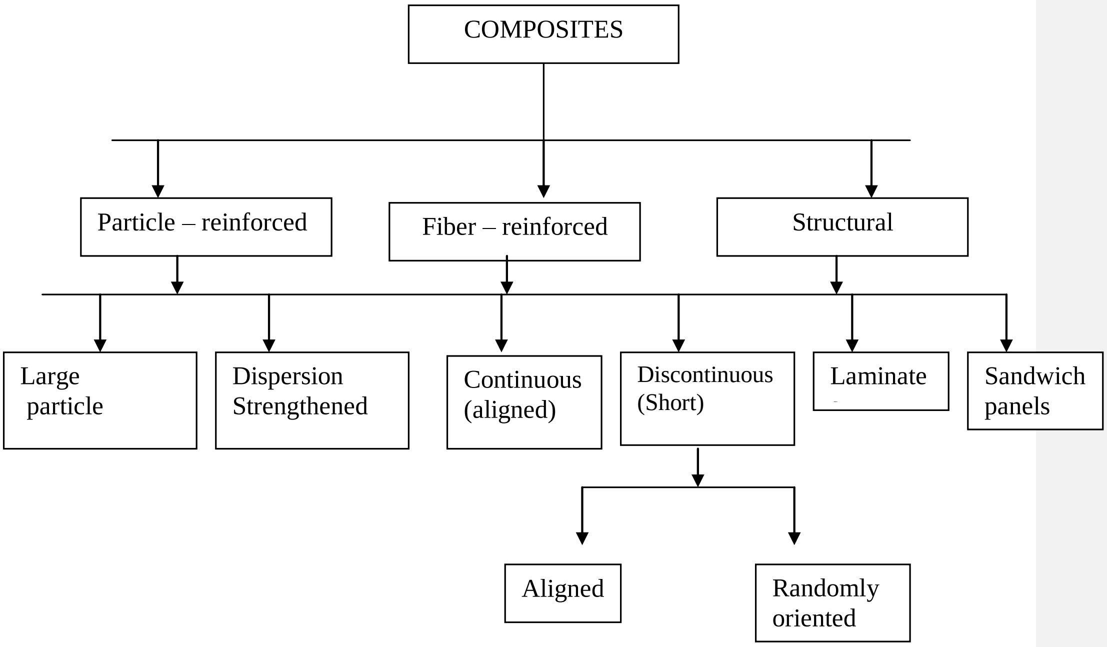

Figure 2.1 – Classification scheme for the various composite types (Callister, 1997).

2.2.3 Types of Reinforcement

Fibers

i. Short fibers with lengths of a few centimeters or fractions of millimeters are felts, mats, and short fibers used in injection molding.
ii. Long fibers which are cut during time of fabrication of the composite material are used as it is or woven. Principal fiber materials are: Glass, Aramid or Kevlar (very light), Carbon (high modulus or high strength), Boron (high modulus or high strength), Silicon carbide (high temperature resistant).

Rupture strength decreases as their diameter increases, and very small fiber diameters allow for effective radius of curvature in fibers bending to be on the order of half a millimeter. However, exception is made for boron fibers (diameters in the order of 100 microns), which are formed around a tungsten filament (diameter = 12 microns). Their minimum radius of curvature is 4mm (Gay, 2002).

The mechanical property or characteristics of a fiber reinforced composite depend not only on the properties of the fiber, but also on the degree to which an applied load is transmitted to the fibers by the matrix phase. Important to the extent of this load transmittance is the magnitude of the interfacial bond between the fiber and matrix phases. Structural composite is normally composed of both homogenous and composite materials the properties of which depend, not only on the properties of the constituent materials but also on the geometrical design of the various structural elements (Gay, 2002).

Particulate

As the name itself indicates, the reinforcement is of particle nature (platelets are also included in this class). It may be spherical, cubic, tetragonal, a platelet, or of other regular or irregular shape, but it is approximately equiaxed. In general, particles are not very effective in improving fracture resistance but they enhance the stiffness of the composite to a limited extent (Pamela, 2007).

Particle fillers are widely used to improve the properties of matrix materials such as to modify the thermal and electrical conductivities, improve performance at elevated temperatures, reduce friction, increase wear and abrasion resistance, improve machinability, increase surface hardness and reduce shrinkage (Pamela, 2007). They have additional advantage over the continuous fiber reinforced PMCs especially since they are low-priced and have both high heat treatment ability and processing flexibility. Particle reinforced PMCs are now being produced commercially (Zhou and Xu, 1987).

2.3 Characteristics and Properties of Composite Materials

The characteristics of composite materials resulting from the combination of reinforcement and matrix depend on: the proportions of reinforcement and matrix, the form of the reinforcement and the fabrication process (Gay, 2002).

Properties of composites are strongly dependent on the properties of their constituent materials, their distribution and the interaction among them. The physical properties of composite materials are generally not isotropic (independent of direction of applied force) in nature, but rather the typically orthotropic (difference depending on the direction of the applied force or load). In contrast, isotropic materials (for example aluminium or steel), in standard wrought forms, typically have the same stiffness regardless of the directional orientation of the applied forces and/or moments (Gay, 2002).

The properties of the composites may be the volume percent sum of the properties of the constituents, or the constituents may interact in a synergistic way resulting in improved or better properties (Pamela et al., 2007). The fabrication process, for example, by powder metallurgy has a different property and characteristic than when produced by casting (double-stirring method, chill casting etc.). Other remarkable properties of composite materials include the following:

a. Composite materials age subject to humidity (epoxy resin can absorb water by diffusion up to 6% of its mass, the composite of reinforcement resin can absorb up to 2%) and heat.
b. Composite materials have a very high corrosion resistance, except in the case of contact "aluminium with carbon fibers" in which case galvanic phenomenon creates rapid corrosion.
c. Composite materials are not sensitive to the common chemicals used in engines: grease, oils hydraulic liquids paints and solvents, petroleum.
d. Composite materials have medium to low level impact resistance (inferior to that of materials).
e. Composite materials have excellent fire resistance as compared with the light alloys with identical thicknesses. However, the smokes emitted from the combustion of certain materials can be toxic.
f. Composite materials are lighter but stronger than their matrix counterparts (Gay, 2002).

2.4 Types of Composites

Composites can be grouped into categories based on the nature of the matrix each type possesses (Ahmed et al., 1999); method of fabrication also varies according to physical and chemical properties of the matrices and reinforced.

2.4.1 Metal Matrix Composites (MMCs)

Metal matrix composites, as the name implies, have a metal matrix. Examples of matrices in such composites include aluminum, magnesium, and titanium. The typical fiber includes carbon and silicon carbide. Metals are mainly reinforced to suit the needs of design. For example, the elastic stiffness and strength of metals can be increased, while large co-efficient of thermal expansion and electric conductivity of metals can be reduced by the addition of fibers such as silicon carbide (Ahmed et al., 1999).

2.4.2 Ceramic Matrix Composites (CMCs)

Ceramic matrix composites (CMCs) combine reinforcing ceramic phases with a ceramic matrix to create materials with new and superior properties (Saheb and Jog, 1999). Ceramic matrix composites (CMCs) have been developed to overcome the intrinsic brittleness and lack of reliability of monolithic ceramics, with a view to introduce ceramics in structural parts used in severe environments, such as rocket and jet engines, gas turbines for power plants, heat shields for space vehicles, fusion reactor first wall, aircraft brakes, heat treatment furnaces etc. It is generally admitted that the use of CMCs in advanced engines will allow an increase of the temperature at which the engine can be operated and eventually the elimination of the cooling fluids, both resulting in an increased yield. Further, the use of light CMCs in place of heavy super alloys is expected to yield significant weight saving.

2.4.3 Polymer Matrix Composites (PMCs)

The most common advanced composites are polymer matrix composites. These composites consist of polymer thermoplastic or thermosetting reinforced by fiber (natural carbon or boron). These materials can be fashioned into a variety of shapes and sizes. They provide a great strength and stiffness along with resistance to corrosion. The reason for these being most common is their low cost, high strength and simple manufacturing principles. Due to the low density of the constituents, the polymer composites often show excellent specific properties (Ahmed et al., 1999). Three types of polymer composites are:

- Fiber reinforced polymer (FRP)
- Particulate reinforced polymer (PRP)
- On multiphase hybrid composites

Fiber reinforced polymer

Common fiber reinforced composites are composed of fibers and a matrix. Fibers are the reinforcement and the main source of strength, while matrix glues all the fibers together in shape and transfers stresses between the reinforcing fibers. The fibers carry the loads along their longitudinal directions. Sometimes, filler might be added to smooth the manufacturing process, impact special properties to the composites, and/or reduce the product cost. Common fiber reinforcing agents include asbestos, carbon/graphite fibers, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminium oxide, glass fibers, polyamide, natural fibers etc. Similarly common matrix materials include epoxy, phenolic, polyester, polyurethane, polyetheretherketone (PEEK), vinyl ester etc (Ahmed et al., 1999).

Fiber reinforced polymer composites are now considered as an important class of engineering materials. They offer outstanding mechanical properties, unique flexibility in design capability and ease of fabrication. Additional advantages include light weight, corrosion and impact resistance and excellent fatigue strength. A fiber reinforced composite is not simply a mass of fibers dispersed within a polymer. It consists of fibers embedded in or bonded to a polymer matrix with distinct interfaces between the two constituent phases.

The fibers are usually of high strength and modulus and serve as the principal load-carrying members. The matrix acts as the load transfer medium between fibers and in less ideal cases where loads are complex, the matrix may even have to partly bear loads. The matrix also serves to protect the fibers from environmental damage before, during and after composite processing. In a composite, both fibers and matrix largely retain their identities and yet result in many properties that cannot be achieved with either of the constituents acting alone. A wide variety of fibers are available for use in composites.

The most commonly used fibers are various types of carbon, glass and aramid. Besides, natural fibers such as jute, sisal and ceramic fibers like alumina, silicon carbide, mullite and silicon nitride are also used in composite making. The unique combinations of properties available in these fibers provide the outstanding functional and structural characteristics such as high specific strength and specific stiffness to the fiber reinforced composites (Anon, 1999).

A key feature of fiber composites that makes them so promising as engineering materials is the opportunity to tailor the materials properties through the control of fiber and matrix combinations and the selection of processing techniques. In principle, an infinite range of composite types exists, from randomly oriented, chopped fiber-based materials at the low property end to continuous, unidirectional fiber composites at the high performance end.

Particle Reinforced Polymer

Particles used for reinforcing include ceramics and glasses such as small mineral particles, metal particles such as aluminium and amorphous materials, including polymers and carbon black. Particles are used to increase the elastic modulus of the matrix and to decrease the ductility of the matrix. Particles are also used to reduce the cost of the composites. Reinforcements and matrices can be common, inexpensive materials and are easily processed. Some of the useful properties of ceramics and glasses include high melting temperature, low density, high strength, stiffness, wear resistance, and corrosion resistance. Many ceramics are good electrical and thermal insulators. Some ceramics have special properties; some ceramics have magnetic materials; some have piezoelectric materials; and a few special ceramics are even superconductors at very low temperatures (Bledzki & Gassan, 1999).

Ceramics and glasses have one major drawback: they are brittle. An example of particle reinforced composites is an automobile tire, which has carbon black particles in a matrix of poly-isobutylene elastomeric polymer. Polymer composite materials have generated wide interest in various engineering fields, particularly in aerospace applications. Research is underway worldwide to develop newer composites with varied combinations of fibers and fillers so as to make them useable under different operational conditions (Anon, 1999). Hard particulate fillers consisting of ceramic or metal particles and fiber fillers made of glass are being used these days to dramatically improve the wear resistance even up to three orders of magnitude (Rusu et al., 2001). Various kinds of polymers and polymer matrix composites reinforced with metal particles have a wide range of industrial applications such as heaters, electrodes, composites with thermal durability at high temperature etc. These engineering composites are desired due to their low density, high corrosion resistance, ease of fabrication, and low cost (Rothon, 1999).

2.5 Strengthening Mechanism of Composites

The strengthening mechanisms of the composites are different and are of a different kind of reinforcing agent morphology such as fibres, particulate or dispersed type of reinforcing elements (Aigbodion & Hassan, 2010).

2.5.1 Strengthening Mechanism of Fibre Reinforced Composite

In such type of composite the reinforcing phase carries the bulk of the load and the matrix transfers the load to the reinforcing phase by the mechanism of seam. The high strength of the reinforcing phase restricts the freee longation of the matrix, especially in its vicinity, whereas the later is free to elongate at some distance away from the former (Clyne, 2001).

This type of non-uniform deformation of the matrix leads to a sheer stress at the matrix reinforcement interface which results in tensile stress at the reinforcing phase. Thus the stress is transferred to the reinforcing phase (Clyne, 2001). The fibers either may be continuous or discontinuous in the matrix. In the former case the load is directly applied to the reinforcing phase and stress is constant over its entire length. Incase of discontinuous fibers, the stress in the fibre increased from zero value at the end to a maximum value in the centre and thus average tensile strength developed is always less than those of continuous fibers.

The strength of the fibre-reinforced composite will be maximum when the fibres are aligned in the direction of the applied stress, i.e. in the isostrain condition. So the strength of this kind of composite depends on the volume percent of the reinforcing element present in the composite, which can be determined by the simple rule of mixtures (Clyne, 2001).

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2.5.2 Dispersion Strengthening Mechanism of Strengthened Composite

In the dispersion-strengthened composite, the second phase reinforcing agents are finely dispersed in the soft ductile matrix. The strong particles restrict the motion of dislocations and strengthen the matrix. Here the main reinforcing philosophy is by the strengthening of the matrix by the dislocation loop formation around the dispersed particles. Thus the further movement of dislocations around the particles is difficult (Hollaway, 1994). Degree of strengthening depends upon the several factors like volume % of dispersed phase, degree of dispersion, size and shape of the dispersed phase, inter particle spacing etc. In this kind of composite, the load is mainly carried out by the matrix materials.

2.5.3 Strengthening Mechanism of Particulate Composite

In the particulate-reinforced composite, the size of the particulate is more than 1µm, so it strengthens the composite in two ways. First, one is that the particulate carries the load along with the matrix materials, and another way is by formation of incoherent interface between the particles and the matrix. So a larger number of dislocations are generated at the interface, thus material gets strengthened. The degree of strengthening depends on the amount of particulate (volume percent), distribution, size and shape of the particulate (Hollaway, 1994).

2.6 Natural Fiber

Natural fiber fillers from agricultural residues and forest products processing are subjected to thermal degradation during polymer composite processing (Bledzki and Gassan, 1999). It is therefore of practical significance to understand and model the decomposition process of the fibers. The model parameters obtained will help estimate the influence of the fiber decomposition on composite properties. Unfortunately, there is still research gap on the suitable models for such a process as well as the model parameters for various fibers.

There are several biomass resources such as bagasse from sugarcane, bark and wood waste, palm waste, corn waste and rice husk. All of these biomass waste can be modified and used as other useful products.

Figure 2.2: Photograph of some natural fibers

In the structural materials area, there is a growing interest in the use of natural/bio-fibers as reinforcing components with petroleum and bio-based thermoplastics and thermosets. Advantages of natural fibers over traditional reinforcing fibers such as glass and carbon are: low cost, low density, acceptable specific properties, ease of separation, enhanced energy recovery and biodegradability. Thermoplastics have the added advantage of recyclability, but thermosets have the necessary mechanical properties for use as structural bio-composites. Even these bio-composites maintain a balance between economics and environment allowing them to be considered for applications in automotives, building, furniture and packaging industries (Bledzki & Gassan, 1999).

A sugar factory produces nearly 30% of bagasse out of its total crushing. Many research efforts have attempted to use bagasse as a renewable feedstock for power generation and for the production of bio-based materials. Bagasse is often used as a primary fuel source for sugar mills when burned in quantity; it produces sufficient heat energy to supply all the needs of a typical sugar mill, with energy to spare. To this end, a secondary use for this waste product is in cogeneration, the use of a fuel source to provide heat energy (Xu & Sun, 2006). Rice husks are the coating for the seeds, or grains, of the rice plant. To protect the seed during the growing season, the husk is made of hard materials, including opaline silica and lignin. The husk is mostly indigestible to humans. Rice husks are a low-cost material from which silicon carbide can be manufactured. The silicon carbide whiskers are then used to reinforce ceramic cutting tools, increasing their strength tenfold (Mishra et al., 1999). Rice is also one of the biomass resources that nowadays have been used as raw material for the research; an example is using rice husk to make light weight aggregate for concrete. Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. Wood is composed of fibre of cellulose (40%–50%) and hemi-cellulose (15%–25%) held together by lignin (15%–30%) (Mishra et al., 1999). Wood chip unsuitable for construction in its natural form may be broken down mechanically (into fibers or chips) or chemically (into cellulose) and used as a raw material for other building materials such as chipboard, engineered wood, hardboard, medium-density fibreboard (MDF), oriented strand board (OSB) (Mishra et al, 1999).

2.6.1 Natural Fibers as Reinforcement

Even though natural fibers have several advantages, certain weaknesses such as poor surface adhesion to hydrophobic polymers, the tendency to form aggregates, not suitable for high temperature application, vulnerability to fungal and pest attack and degradation by moisture greatly reduce the potential of these fillers to be used as reinforcement (Mishra et al., 1999). These drawbacks, especially incompatibility of fillers with the polymer matrix lead to low filler-matrix interfacial bonding strength and poor wetting of the fillers by the matrix resin which can lead to reduction in mechanical properties of the composites.

Therefore, surface modification by the use of coupling or modifier agents is commonly suggested as solution to overcome the drawbacks of lowered strength property (Bledzki & Gassan, 1999). One of the natural fillers that has been tried was banana pseudo-stem (BPS) fibre. BPS is one of the natural fillers obtained from banana trunk. The incorporation of BPS as a reinforcing component in the polymer composites has received much attention (Sun et al., 2004).

Most of the research works on BPS so far dealt with polymers such as polyester, polystyrene and phenol-formaldehyde resin. The researchers focused on the effect of filler loading, filler particle size distributions and filler treatment on the mechanical properties of the composites. Most researchers have used wood flour, wood sawdust, rice husk as handbag and as fillers in polymer matrix (Xu & Sun, 2006). The use of these fillers in the polymer matrix yields products that are more brittle than neat polymer. The incorporation of the natural fillers alters the ductile mode of failure of the matrix. The brittleness of PVC/woodfillers composite compared to the unfilled PVC may prevent this emerging class of materials from capturing their full market potential in applications such as door and window panels. One of the most important aspects in the development of polymer compound by using fillers is to achieve a good combination of properties and process-ability at a moderate cost.

Cellulosic fibers like BPS, sisal, palms, bamboo, wood in their natural condition, as well as several waste cellulosic products such as shell flour, wood flour and pulp have been used as reinforcement agents of different thermosetting and thermoplastic (Wasylciw, 1999). Unlike the traditional engineering fibers like glass and carbon fillers, along with mineral fillers, these lingo cellulosic fillers are able to impart to the composite certain benefits such as low density, less machine wear; biodegrability; minimal health hazards; and a high degree of flexibility (Mishra et al., 1999).

2.6.2 Classification of Natural Fibers

Wasylciw (1999) classified natural fibers in two broad categories: non-wood fibers and wood fibers.

- Non-wood fibers are divided into straw like corn, wheat and rice straw; bast like kenaf (Hibiscus cannabicus), flax (Linumusitatissimum), jute (Corchorus), ramie (Boehmeria nivea), and hemp (Cannabis sativa); seed/fruit like sisal (Agave sisalana), pineapple (Ananas comosus) leaf, and henequen (Agave fourcroydes) fibers; grassfibers like bamboo fibre, switch grass(*Panicumvirgatum*), and elephant grass (*Erianthus elephantinus*). Natural fibers in the form of wood flour have also been often used for preparation of natural fiber composites (Wasylciw, 1999). The characteristic values of natural fillers vary from one fiber to another. Some of the characteristic values are the cellulose content in the fillers, the degree of polymerization of the cellulose and the microfibrils angle fibers. Higher cellulose content, higher degree of polymerization and a lower microfibrillar angle will have higher tensile strength and modulus. The variations in the characteristic value exhibit the variations in mechanical properties both along the length of an individual fiber and between fibers (Wasylciw, 1999).

The fibers which serve as a reinforcement in reinforced plastics may be synthetic or natural. Although glass and other synthetic fiber-reinforced plastics possess high specific strength, their fields of application are very limited because of their inherent higher cost of production. Some of these natural fillers are not only strong and light-weight but also relatively very cheap (Xu & Sun, 2006). The specific properties of the natural fillers composites were in some cases better than those of glass (Table 2.1). This suggests that natural fibers composites have a potential to replace glass in many applications that do not require very high load bearing capabilities.

Table 2.1. A comparison between natural and glass fibers (Xu and Sun, 2006)

Property	Natural fibers	Glass fibers
Density	Low	Twice that of natural fibers
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO_2 neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not biodegradable

Natural fibers include those made from plant, animal and mineral sources. Natural fibers can be classified according to their origin (Xu and Sun, 2006).

- Animal fibers
- Mineral fibers
- Plant fibers

Animal Fiber

Animal fibers generally are comprised of proteins; examples: mohair, wool, silk, alpaca, angora.

- **Animal hair (wool or hair)**: Fiber taken from animals or hairy mammals. E.g. Sheep wool, goat hair (cashmere, mohair), alpaca hair, horse hair etc.
- **Silk fibers**: Fiber collected from dried saliva of bugs or insects during the preparation of cocoons. Examples include silk from silk worms.
- **Avian fibers**: Fibers from birds, e.g. feathers and feather fiber (Bledzki and Gassan, 1999).

- **Mineral fiber**

Mineral fibers are naturally occurring fiber or slightly modified filler procured from minerals. These can be categorized into the following categories:

Asbestos: This is the only naturally occurring mineral fibers. Variations are serpentine and amphiboles, anthophyllite.

Ceramic fibers: Glass fibers (Glass wood and Quartz), aluminum oxide, silicon carbide, and boron carbide.

Plant fiber

Plant fibers are generally comprised mainly of cellulose: examples include cotton, jute, flax, ramie, sisal and hemp. Cellulose fibers serve in the manufacture of paper and cloth. This fiber can be further categorized into following.

Seed fiber: Fibers collected from the seed and seed case, e.g. cotton and kapok.

Leaf filer: Fibers collected from the leaves, e.g. sisal and agave.

Skin fiber: Fibers collected from the skin or bast surrounding the stem of their respective plant. These fibers have higher tensile strength than other fibers. Therefore, these fibers are used for durable yarn, fabric, packaging and paper. Some examples are flax, jute, banana, hemp, and soybean.

Fruit filler: Fibers collected from the fruit of the plant, e.g. coconut (coir) fiber.

Stalk filler: These fibers are actually the stalks of the plant, e.g. straws of wheat, rice, barley, and other crops including bamboo and grass. Tree wood is also such a fiber.

The natural fibers can be used to reinforce both thermosetting and thermoplastic matrices. Thermosetting resins such as epoxy, polyester, polyurethane, phenolic etc. are commonly used today in natural fiber composites requiring higher performance applications. They provide sufficient mechanical properties, in particular stiffness and strength, at acceptably low price levels. Considering the ecological aspects of material selection, replacing synthetic fibers by natural ones is only a first step. Restricting the emission of green house effect causing gases such as CO_2 into the atmosphere and an increasing awareness of the finiteness of fossil energy resources are leading to developing new materials that are entirely based on renewable resources (Bledzki AK, Gassan, 1999).

2.6.3 Applications of Natural Fiber Composites

The natural fiber composites can be very cost effective material for the following applications (Bledzki & Gassan, 1999):

- Building and construction industry: panels for partition and false ceiling, partition boards, wall, floor, window and door frames, roof tiles, mobile or pre-fabricated buildings which can be used in times of natural calamities such as floods, cyclones, earthquakes etc.
- Storage devices: post-boxes, grain storage silos, bio-gas containers etc.
- Furniture: chair, table, shower, bath units etc.
- Electric devices: electrical appliance, pipes etc.
- Everyday applications: lampshades, suitcases, helmets etc.
- Transportation: automobile and railway coach interior, boat and toys

The interest in natural fillers-reinforced polymer composite materials is rapidly growing both in terms of their industrial applications and fundamental research. They are renewable, cheap, completely or partially recyclable, and biodegradable. Plants such as flax, cotton, hemp, jute, sisal, kenaf, pineapple, ramie, bamboo, banana etc. as well as wood, used from time immemorial as a source of lignocellulosic fillers, are more and more often applied as the reinforcement of composites. Their availability, renewability, low density, and price as well as satisfactory mechanical properties make them an attractive ecological alternative to glass, carbon and man-made fibers used for the manufacturing of composites (Sun et al, 2004).

The natural fiber-containing composites are more environmental friendly, and are used in transportation (automobiles, railway coaches, aerospace), military applications, building and construction industries (ceiling paneling, partition boards), packaging, consumer products etc.

2.6.4 Basic Mechanical Properties of Composite Materials

The basic mechanical properties are an important influence on the load-bearing ability and structural performance of the material. Load-bearing ability means that the material has adequately high values of strength, modulus and ductility under a loading condition that is relevant to the application (Callister, 1997). A particularly common loading condition for a composite panel or slab is bending (flexure). For example, when a wing of an aircraft is hit by a bird during flight, bending is involved; it is also involved when the floor of an aircraft is hit by a heavy falling object (such as a hammer) and when a car is traveling on a bridge (bending of the bridge deck) (Callister, 1997). During flexure, one surface is under tension while the opposite surface is under compression, as illustrated in Fig. 2.6. For a concrete column, the important loading condition is compressive, with the stress occurring along the axis of the column, although flexural loading can also occur, as in the case of a car hitting the column. When mechanical properties are described without indicating the loading condition, they usually refer to the tensile case, with the exception of brittle materials (such as cement-matrix composites), for which the compressive case is dominant due to the fact that the compressive strength is much higher than the tensile strength for a brittle material (Callister., 1997).

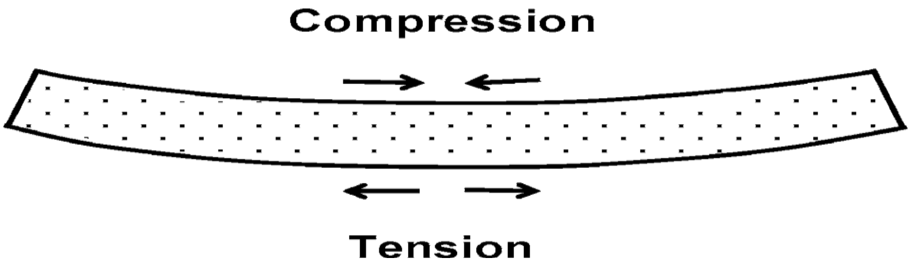

Figure 2.6: Tension and compression on the opposite sides of a beam under flexure

2.6.4.1 Modulus of elasticity

The modulus of elasticity describes the resistance to elastic deformation, which is reversible (Kinoch et al., 1985). One common mechanism of elastic deformation under tension is bond stretching, when the load is released, the dimension returns to its original value. The stress–strain curve is linear in the elastic regime. This linear relation constitutes Hooke’s Law, which states that stress is proportional to strain, with the proportionality constant being the modulus (Kinoch et al., 1985). The modulus is given by the slope of the linear region; i.e., it is the stress per unit strain in the elastic regime, as illustrated in Fig. 2.7. To emphasize that it is obtained from the slope of the curve, this modulus is also called the tangent modulus. When dynamic strain around an operating point outside the elastic regime is relevant to a particular application, the relevant tangent modulus is obtained by finding the slope at the operating point, as shown in Fig. 2.7.

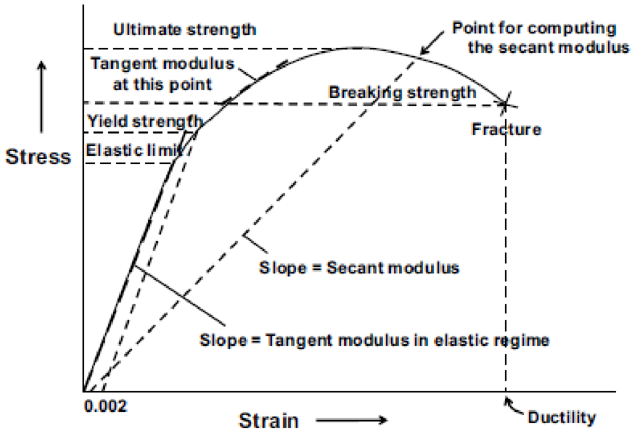

Figure 2.7: Stress-strain curve illustrating the meaning of the tangent modulus, the secant modulus, the elastic limit, the 0.2% offset yield strength, the ultimate strength, and the breaking strength.

2.6.4.2 Strength

There are a number of strength parameters. The highest stress in a stress-strain curve up to failure is the ultimate strength, which is called the tensile strength in the case of tensile loading. The stress at fracture (failure) is called the breaking strength, which can be lower than the ultimate strength (Fig. 2.3) due to the occurrence of necking during plastic deformation prior to failure. The elastic limit is the stress at which the stress-strain curve starts to deviate from linearity, although this point on the curve cannot be clearly identified in most cases. The stress above which plastic deformation occurs is called the yield strength (Callister, 1997). A construction is conventionally used to help identify the yield strength. In this construction, a straight line that is parallel to the initial straight line portion of the stress-strain curve and that intersects with the strain axis at 0.002 (or 0.2%) is drawn (Fig. 2.7). The intersection of this straight line with the stress-strain curve defines the yield strength. Upon unloading from the stress equal to this yield strength, a strain of 0.002 is obtained when the stress has returned to zero. Therefore, this yield strength is called the 0.2% offset yield strength. The value of 0.2% is chosen because this value, when applied to metals, usually gives a yield strength value that is close to the minimum stress required for plastic deformation. The yield strength is important for engineering design, as most engineering components are only designed to operate in the elastic regime so that there is no permanent change in dimensions during the use of the component. Plastic deformation may involve not only a permanent change in dimensions but also a change in the microstructure (such as the dislocation density), which affects the strength, modulus and ductility of the material. The ultimate strength is also useful, as it relates to the highest stress that a material can withstand without breaking. When the term “strength” is used without qualification, it usually refers to the ultimate strength (Callister, 1997).

2.6.4.3 Ductility

Ductility refers to the maximum strain in the stress-strain curve (Fig. 2.7). A brittle material undergoes little or no plastic deformation before failure, whereas a ductile material undergoes considerable plastic deformation before failure. Hence for a highly brittle material, failure occurs at the end of the elastic regime, with no plastic deformation prior to failure. This also means that for a brittle material, damage can occur within the elastic regime. Thus, the use of a brittle material should be limited to the low-stress portion of the elastic regime (Callister, 1997).

2.6.4.4 Brittle vs. Ductile Materials

A brittle material tends to have microcracks that propagate under tension in the direction perpendicular to the plane of the crack. Under compression in this direction, the crack just closes to a certain degree. As a result, a brittle material breaks much more easily under tension than under compression, so that the tensile strength is lower than the compressive strength and the tensile ductility is lower than the compressive ductility (Fig. 2.8). On the other hand, the compressive and tensile moduli can be comparable, as elastic deformation does not involve crack propagation (Callister, 1997). Because of its low tensile strength, a brittle material is preferably used under compression rather than tension, and the part of a brittle material that is expected to encounter a tensile stress needs to be reinforced. This is why the reinforcement of concrete (a brittle material) with embedded steel rebars is widely used, with the rebars positioned at the part of the concrete component that encounters tensile stress. For example, a concrete beam under flexure is reinforced with steel rebars, particularly in the half of the beam that encounters tension (i.e., the lower half of the beam in Fig. 2.8).

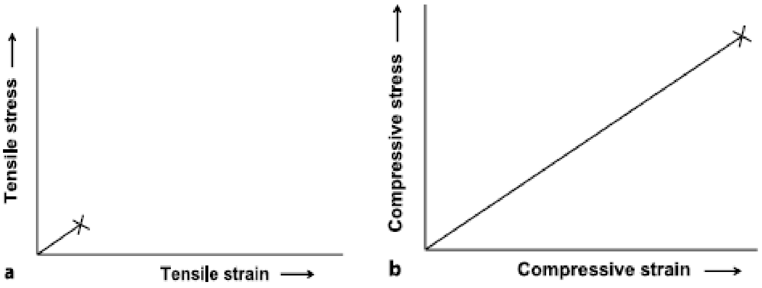

Figure 2.8Stress–strain curves of a brittle material: **a** under tension; **b** under compression

2.6.4.5 Strengthening

Conventional strengthening methods, such as the use of alloying (e.g., the formation of a solid solution), tend to increase the strength and modulus but decrease the ductility. Thus, a material of high strength and modulus tends to be brittle. However, strengthening through the use of a filler can result in increases in strength, modulus and ductility (all at the same time) when the filler is a fibre that is well bonded to the matrix and when the matrix is brittle. When the matrix is ductile, as is the case for a polymer matrix, filler addition tends to decrease the ductility. However, when the matrix is brittle, as is the case of cement, carbon or ceramic matrix filler addition tends to increase the ductility because of the mechanism of fibre pull-out. The increase in modulus due to the use of filler occurs whenever the filler has a higher modulus than the matrix and the bonding between the filler and the matrix is not too weak (Bahad et al., 1993). The increase in strength due to the use of filler requires that the bonding between the filler and the matrix is sufficiently strong, as a weak interface will act as a crack initiation site. Thus, it is much easier to use a filler to increase the modulus than to increase the strength. When the interface is weak, the modulus may increase with increasing filler content, while the strength may decrease with increasing filler content. This is why interface tailoring is critical to composite engineering. When the filler has nanoscale dimensions, the interface area is large and interface tailoring becomes even more important (Bahad et al., 1993).

2.6.4.6 Bending/flexural strength

This is used to test the strength of the material under an applied bending load. This is usually carried out by supporting the plastic at its two ends and applying a midpoint load, as shown in Figure 2.9 below, until the material is broken. The max. bending load is then recorded.

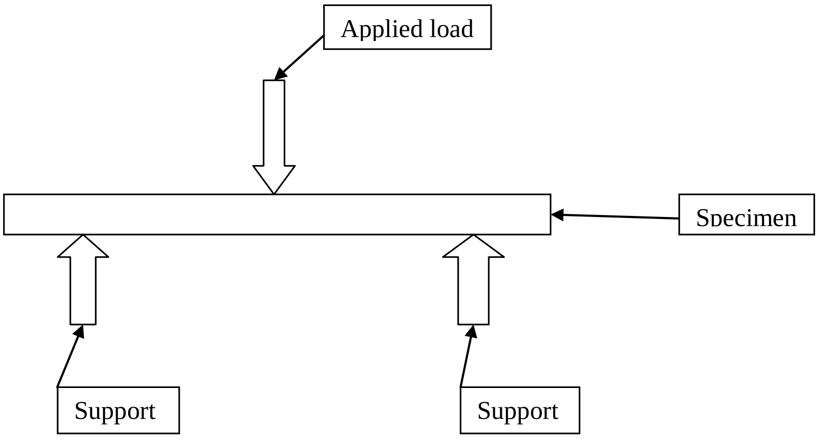

Fig. 2.9: Schematic representation of how bend test is carried out.

The flexural strength is related to the load at which the specimen ruptures by the following formula (Hollaway, 1994):

$$\text{Flexural strength} = \frac{3(load)(span)}{2(width)(thickness^2)} \qquad (2.1)$$

2.7 Origin of the Mortar

The word comes from Latin word *mortarium* meaning *crushed*. Mortar is a workable paste used to bind construction blocks together and fill the gaps between them. Mortar may be used to bind masonry blocks of stones, bricks, cinder blocks etc. Mortar becomes hard when it sets, resulting in a rigid aggregate structure. Modern mortars are typically made from a mixture of sand, a binder such as cement or lime, and water. Mortar can also be used to fix, or repoint, masonry when the original mortar has washed away (ACI 2 lOR, 1994).

Comment [Kingsley3]: Is this the right word here?

2.7.1 Cement

Cement has been used for centuries. In 1824 the first powder was made from limestone and clay to form what we now know as Portland cement. Cement is essentially calcium-based. Calcium cement is made from lime ($CaCO_3$). Another is made from gypsum

($CaSO_4.2H_2O$). Lime cements include Portland cement and natural cements. The gypsums include plaster of Paris, hard-finish plaster, and gypsum wallboard. These cements are used in thin layers to protect masonry, or as a binder of stone, brick, or aggregate (Bye, 1983).

2.7.2 Chemical Composition of Portland Cement

There are four chief minerals present in ordinary Portland cement: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_5$) and calcium alumina ferrite ($Ca_4Al_nFe_{2-n}O_7$). The formula of each of these minerals can be broken down into the basic calcium, silicon, aluminum and iron oxides (Table 2.5). Cement chemists use abbreviated nomenclature based on oxides of various elements to indicate chemical formulae of relevant species, i.e., C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3. Hence, traditional cement nomenclature abbreviates each oxide as shown in Table 2.2 (Bye, 1983).

Table 2.2: Chemical formulae and cement nomenclature for major constituents of Portland cement

Mineral	Chemical formula	Oxide composition	Abbreviation
Tricalcium silicate (alite)	Ca_3SiO_5	$3CaO.SiO_2$	C3S
Dicalcium silicate (belite)	Ca_2SiO_4	$2CaO.SiO_2$	C2S
Tricalcium aluminate	$Ca_3Al_2O_4$	$3CaO.Al_2O_3$	C3A
Tetracalcium aluminoferrite	$Ca_4Al_nFe_{2-n}O_7$	$4CaO.Al_nFe_{2-n}O_3$	C4AF

Abbreviation notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3.

The composition of cement is varied depending on the application. A typical example of cement contains 50–70% C3S, 15–30% C2S, 5–10% C3A, 5–15% C4AF, and 3–8% other additives or minerals (such as oxides of calcium and magnesium). It is the hydration of the calcium silicate, aluminate, and aluminoferrite minerals that causes the hardening, or setting, of cement. The ratio of C3S to C2S helps to determine how fast the cement will set, with faster setting occurring with higher C3S content. Lower C3A content promotes resistance to sulfates. Higher amounts of ferrite lead to slower hydration. The ferrite phase causes the brownish gray colour in cement, so that “white cement” (i.e., the one low in C4AF) is often used for aesthetic purposes (Bye, 1983). The calcium aluminoferrite (C4AF) forms a continuous phase around the other mineral crystallites, as the iron-containing species act as a fluxing agent in the rotary kiln during cement production and are the last to solidify around the others. Figure 2.9 shows a typical cement grain.

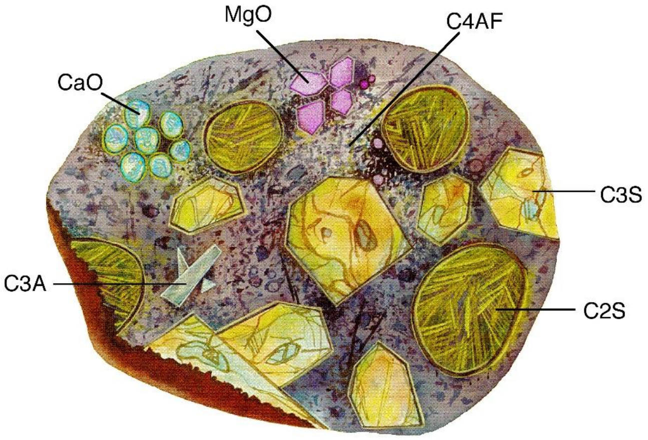

Figure 2.10: A pictorial representation of a cross-section of a cement grain

(Adapted from Bye, 1983)

It is worth noting that a given cement grain will not have the same size or even necessarily contain the same minerals as the next grain. The heterogeneity exists not only within a given particle, but extends from grain to grain, batch-to-batch, plant to plant.

2.7.3 Lime

Limestone is calcium carbonate (calcite) with the chemical symbol $CaCO_3$. In another raw state, magnesium carbonate ($MgCO_3$) is also present in substantial amounts. In general, magnesium aids in the purification of lime. Impurities, such as alumina, silica, and iron oxide, are also present. These impurities may be harmful to the production of purified lime. The purification process consists of controlled heating of the raw materials to between 1650^o and 1800^{o}F, after it has been crushed by grinding and fed into furnaces. This process, known as calcining, causes the dissociation of the calcium carbonate into quicklime (CaO) and carbon dioxide (CO_2) (Herman, 1973). If magnesium carbonate is present, it will also dissociate into magnesia (MgO) and carbon dioxide (CO_2). The equation may be written as:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

$$MgCO_3 + \text{heat} \rightarrow MgO + CO_2 \text{ (Shetty, 2003)}$$

The resulting lime is sold as pulverized, lump, or screened lime. Sometimes lime is mixed with controlled amounts of water, pulverized, and sold as slake or hydrated lime. The calcined lime when slaked increases in volume and generates much heat. The equation is:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat (Shetty, 2003).}$$

This type of lime is marketed in the form of a fine white powder. Also present is the calcined magnesia (MgO) that is not slaked. It must be removed; otherwise, it will cause cracks, since it will slake very slowly and expand after the cement has set. When lime hardens, it does so by absorbing carbon dioxide from the air. In the presence of water and CO_2, calcium carbonate re-forms. As the calcium carbonate crystals re-form, they interlock, causing solidification. The equation is:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

If water is added to the quicklime in greater amounts than needed, $Ca(OH)_2$ forms as a paste. The same thing happens to slaked lime. The exposure of the paste to the air causes the

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$Ca(OH)_2$ to revert to calcium carbonate. If too much water is used, particles of water will remain in the structure after solidification. If quicklime is to be used as a cementing material, it must be hydrated by slaking. After several weeks the slaked lime is ready for use. Hydrated lime may be used immediately. Lime may be used as a plastering material. It is mixed four parts sand to one part lime and used as a plaster. It is slow setting. It is also used in agriculture as a soil reconditioner. It has a compressive strength of about 400psi (Barbara et al, 2007).

Besides being used as an ingredient in plaster and mortar, lime may be mixed and used as a lime-cement mortar, which has high strength than lime mortar, but not the strength of cement mortar. The mixture for lime-cement mortar is generally two parts lime, one part cement, and six parts sand. The mixture is brought to a thick consistency by adding water. Lime plaster produces a rough-finish plaster. The ingredients are one part lime and three parts sand. A hard plaster may be produced by mixing two parts plaster of Paris with one part lime (Barbara et al, 2007).

2.7.4 Gypsum

Gypsum in its raw, pure state is white. In its impure state, it contains some limestone, silica, and alumina and is light gray. Its chemical symbol is $CaSO_4.2H_2O$. The process of refining raw gypsum consists of heating it to drive off the two parts of water, as indicated in the equations (Barbara et al, 2007):

$$CaSO_4.2H_2O \rightarrow CaSO_4\tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O \qquad \text{at about } 240^{o}F$$

$$CaSO_4.\tfrac{1}{2}H_2O \rightarrow CaSO_4 + \tfrac{1}{2}H_2O \qquad \text{at about } 390^{o}F$$

This process is called the calcination of raw gypsum. The material is control heated in large kettles or in almost horizontal kilns. When the horizontal kiln is used, the material is fed into the end of the kiln and rotated. The gypsum works its way down the kiln and out from the other end. The end product of the 390^oF stage yields $2CaSO_4.H_2O$, which is called plaster of Paris. This material is used in wallboard, rock lath, sheathing, plastering, and moulds for casting dental and medical materials. It is used with lime to produce a finished plaster. Sometimes other materials, such as lime or clay, are present in plaster of Paris. If mixed with water, the end product is called wall plaster or cement plaster. When mixed with sawdust or general cinders, the aggregate is cast into blocks and used as a building material. Firm setting is caused by interlocking crystallization (Barbara et al., 2007).

When the temperatures of calcinations exceed 390^oF, all the water is driven off, and the $CaSO_4$ remains. This is called flooring plaster. When alum or borax is added, the workability of the plaster is increased. This is called hard-finish plaster. Keene’s cement results when alum is added to calcinated gypsum and recalcinated. After it is ground, it is ready for use. This is a very hard gypsum product which sets in about 3 hours (Barbara et al., 2007). When mixed with water, the half-hydrate and the anhydrite of gypsum will re-form into a hard interlocking phase of the original $CaSO_4.2H_2O$. The taking on of water and subsequent hardening, or setting, classifies plaster of Paris as hydraulic cement. Impurities, such as glue and borax, will slow down the setting process. Warm water will increase the setting time. The strength of plaster is increased by adding hair or wood fibres to the product. Its ultimate strength is a function of the water-to-plaster ratio. Excess water weakens the final product (Barbara et al., 2007).

2.7.5 Categories of Mortar

2.7.5.1 Portland Cement Mortar

Portland cement mortar (often known simply as cement mortar) is created by mixing ordinary Portland cement (OPC), hydrated lime, and aggregate (or sand) with water. It was invented in 1794 by Joseph Aspdin and patented on 18 December 1824, largely as a result of various scientific efforts to develop stronger mortars than existed at the time. It was made popular during the late nineteenth century, and owing to the First World War, it had by 1930 superseded lime mortar for new constructions. The main reasons for this were that Portland cement sets hard and quickly, allowing a faster pace of construction, and requires fewer skilled workers. However, as a general rule, Portland cement should not be used for the repair or repointing of older buildings constructed in lime mortar, which require the flexibility, softness and breathability of lime if they are to function correctly (Standard Specification for Portland Cement, 1999).

2.7.5.2 Polymer Cement Mortar

Polymer cement mortars (PCM) are the materials which are made by partially replacing the cement hydrate binders of conventional cement mortar with polymers. The polymeric admixtures include latexes or emulsions, redispersible polymer powders, water-soluble polymers, liquid resins and monomers. It has low permeability, and it reduces the incidence of drying, shrinkage and cracking, mainly designed for repairing concrete structures.

2.7.5.3 Pozzolana Mortar

Pozzolana is a fine, sandy volcanic ash, originally discovered and dug in Italy at Pozzuoli in the region around Mount Vesuvius, but later at a number of other sites. The Romans learned that pozzolana added to lime mortar allowed the lime to set relatively quickly and even under water, and the ancient Roman architect Vitruvius speaks of four types of pozzolana. It is found in all the volcanic areas of Italy in various colours: black, white, grey and red. Pozzolana has since become a generic term for any siliceous and/or aluminous additive to slaked lime to create hydraulic cement. Finely ground and mixed with lime, hydraulic cement, like Portland cement, makes a strong mortar that will also set under water (Toleˆdo Filho et al., 2000).

2.7.5.4 Firestop Mortar

Firestop mortars are mortars most typically used to firestop large openings in walls and floors required to have a fire-resistance rating. They are passive fire protection items. Firestop mortars differ in formula and properties from most other cementitious substances and cannot be substituted with generic mortars without violating the listing and approval use and compliance. Firestop mortar is usually a combination of powder mixed with water, forming a cementatious stone which dries hard. It is sometimes mixed with lightweight aggregates, such as perlite or vermiculite. It is sometimes pigmented to distinguish it from generic materials in an effort to prevent unlawful substitution and to enable verification of the certification listing. In the broadest sense, cementing materials are those which bind other materials. Mortar is such a material. It is used for bedding and bonding brick, stone, tile etc. It should contain as much water as is consistent with the troweling operation. Since the water content determines the quality of the bond achieved, the water content should be high (Toleˆdo Filho et al., 2000).

2.7.5.5 Lime Mortar

The speed of set can be increased by using impure limestone in the kiln to form hydraulic lime that will set on contact with water. Such a lime must be stored as a dry powder. Alternatively, a pozzolanic material such as calcined clay or brick dust may be added to the mortar mix. This will have a similar effect of making the mortar set reasonably quickly by reaction with the water in the mortar (Toleˆdo Filho et al., 2000).

Using Portland cement mortars in repairing older buildings originally constructed using lime mortar can be problematic. This is because lime mortar is softer than cement mortar, allowing brickwork a certain degree of flexibility to move to adapt to shifting ground or other changing conditions. Cement mortar is harder and allows less flexibility. The contrast can cause brickwork to crack where the two mortars are present in a single wall (Savastano Jr et al., 2001).

Lime mortar is considered breathable in that it would allow moisture to freely move through it and evaporate from its surface. In old buildings with walls that shift over time, there are often cracks which allow rain water into the structure. The lime mortar allows this moisture to escape through evaporation and keeps the wall dry. Re-pointing or rendering an old wall with cement mortar stops this evaporation and can cause problems associated with moisture behind the cement (Savastano Jr et al., 2001).

2.8 Use of Polymers in Concrete

Although the physical properties and relatively low cost make Portland cement concrete, the most viable construction material, it is not without limitations. Some of the major ones have been listed below (Priya & Paul, 2002):

a. Low flexural strength;

b. Low failure strain;

c. Susceptibility to frost damage; and

d. Low resistance to chemicals.

These drawbacks are well recognized and can usually be accommodated in most applications. In certain situations, these problems can be solved by using materials which contain an organic polymer or resin instead of or in conjunction with Portland cement. These relatively new materials offer the advantages of higher strength, improved durability and good resistance to corrosion, reduced water permeability and greater resistance to damage from freeze-thaw cycles.

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Naturally available polymers such as bitumen, glutinous rice paste, molasses etc. have been used to enhance the properties of the existing building materials. The first patent on the use of natural rubber as an additive for paving material was issued to Cresson in 1923 (Priya & Paul, 2004). Ever since then, considerable research in this field has been conducted. Moreover, durability of the building structure has been reduced due to ever-increasing chemical pollution in the environment (Priya & Paul, 2002). In 1930s, rubber latexes like natural rubber, poly (styrene-butadiene) (SBR), poly (acrylonitrile-butadiene), polychloroprene (CR) were used for the preparation of polymer cement concrete. Thermoplastics such as polyvinylacetate, acrylics and vinylidine chlorides, introduced in the 1960s, had greater strengthening effects on the mortars than elastomers. Polymer concrete (Priya et al., 2005) made by blending various polymers with cement, enhances workability, durability and strength of the cement concrete structures. Some of the polymeric admixtures now used extensively in civil engineering are in the form of adhesives, modifiers and matrix materials. Among the various types of composites of polymers and cement, polymer concrete is increasingly used in construction and repair of highways and bridges and in the manufacturing of various kinds of precast articles. The cement mortars or concrete that are modified by polymers are called Polymer modified mortar (PMM) or Polymer modified concrete (PMC).

2.8.1 Polymers as Cement Admixtures

Polymers as admixtures to cement may be classified into four categories depending on the particle size and form. These may be added to the cement as latexes, redispersible powders or emulsions, water-soluble polymers or liquid polymers (Priya & Paul, 2002).

2.8.1.1 Polymer Latexes or Dispersions

These polymers are in the form of particles of 0.05-5 /lm diameter dispersed in water. Polymer latexes are classified into cationic, anionic and nonionic depending on the charges borne by the polymer particles. Apart from the polymer particles, they consist of emulsifiers, different monomers and stabilizers. The total solid content is about 40–50% by mass. Some of the requirements for the polymer latexes to be used as admixtures are (Priya and Paul, 2004):

i. They should have high stability in the presence of calcium and aluminium ions present in the cement during its hydration. They must also have good mechanical stability during the mixing and processing of the cement concrete and mortar.

ii. They must not have adverse influence on the hydration. The polymer latexes must form polymer films in the concrete or mortar and must adhere on the cement hydrates and aggregates.

iii. They must possess good water and alkali resistance in the presence of the alkaline cement environment. They must also have high thermal stability.

iv. Some of the latexes used in the present study are SBR, NBR, PV AC, polyacrylic and polyacrylic styrene.

2.8.1.2 Redispersible Polymer Powders

These are manufactured in a two-step process – firstly, the polymer latexes are made by emulsion polymerization and then spray-dried to obtain polymer powders. These are dry blended with cement followed by wet mixing with water (Priya & Paul, 2002).

2.8.1.3 Water Soluble Powders

These are mostly water soluble powdered polymers. Cellulose derivatives, polyvinyl alcohol and polyacrylamide form some of the typical examples. These are added to the cement concrete or mortar in the form of powders or aqueous solutions during mixing. When added as a powder they are blended with the cement – aggregate mix before adding water (Priya & Paul, 2004).

2.8.1.4 Liquid Polymers

Liquid polymers are viscous polymeric substances such as epoxy resin and unsaturated polyester resin mixed with an accelerator and a hardener or acatalyst. The above mixture is added to the cement mortar or concrete during mixing (Priya & Thachil, 2007).

2.9 Cement Concrete-Polymer Composites

Cement concrete-polymer composites are classified into three types depending on their process technology (Priya and Thachil, 2007).

a) Polymer modified cement concrete (PMC) and Polymer modified mortar (PMM)

Portland cement mortar (often known as cement mortar) is made by mixing Portland cement with sand and water. PMM and PMC are composite materials made by partially replacing and strengthening the cement hydrate binders of conventional mortar and concrete with polymeric modifiers or admixtures such as polymeric latexes or dispersions, redispersible powders, water soluble powders, liquid resins and monomers. This type has a monolithicco-matrix in which the organic polymer matrix and cement gel matrix are homogenized. The properties of PMM and PMC are characterized by such a co-matrix. When the modification is due to polymer latexes, water-soluble polymers or redispersible powders, the water in the admixture is used for cement hydration and a polymer film is formed. When liquid resins or monomers are used, the water added is taken up for the cement hydration and polymerization of the liquid resins, or monomers takes place in situ (Priya and Thachil, 2007).

2.9.1 Process Technology

The process technology of PMC and PMM is the same as that of conventional cement mortar and concrete. The polymeric modifiers are added to the cement concrete while mixing and cured under optimum conditions. The types of cement employed for the manufacture of these composites depend on the application.The mix designs of this type, though similar to the conventional ones, depend on the workability, strength, adhesion, waterproofness and chemical resistance requirements. The above properties are mostly dependent on the polymer cement ratio rather than the *W/C* ratio. The polymer cement ratio *(PlC)* is defined as

PlC = {(weight of polymer) *I* (weight of cement used in the PMM *IPMC)}*

In the case of polymer latexes, the numerator is the weight of the total solid content of the latex; whereas for redispersible polymer powders, water soluble powder, liquid resins and monomers, and the actual weight of the polymer are used. Normally the *PlC* ratio is 5-15% and *W/C* ratio is in the range 30-50%. The latex is diluted by blending it with water and then it is added to the cement. The mix time is so selected as to avoid entrapment of air. The redispersible powders and water-soluble powders are dry mixed with the cement before the addition of water (Priya & Thachil, 2007).

2.9.2 Principles of Polymer Modification

I) ***Latex modification****:* In latex modified mortar and concrete both cement hydration and polymer film formation take place yielding a monolithicmatrix phase with a network structure in which the cement hydrate and polymer phase interpenetrate each other. Some chemical reactions may take place between the cement and the polymer phases. Ohama's (2006) theory explains the co-matrix formation as a three-step model. In the first stage, the polymer latexes are mixed with fresh cement mortar and concrete to form a uniformly dispersed cement paste phase. In this paste the cement gradually undergoes hydration and the polymer particles deposit partially on the surfaces of unhydrated and hydrated cement particle mixtures. In the second stage, the cement hydration takes place using the water present in the capillary pores as a result of which the polymer particles flocculate to form a continuous, close-packed layer on the surfaces of unhydrated cement and hydrated cement gel. Some chemical reactions may take place between the particle surfaces of the reactive polymers such as poly acrylic esters (PAE) and poly (vinylidenechloride - vinyl chloride) and Ca2+ ions from Ca(OHh or silicate ions on surfaces of the aggregates. Such reactions (Figure 2.11) improve the properties of hardened latex-modified mortar and concrete (Bing Chen & Juanyu Liu, 2007).

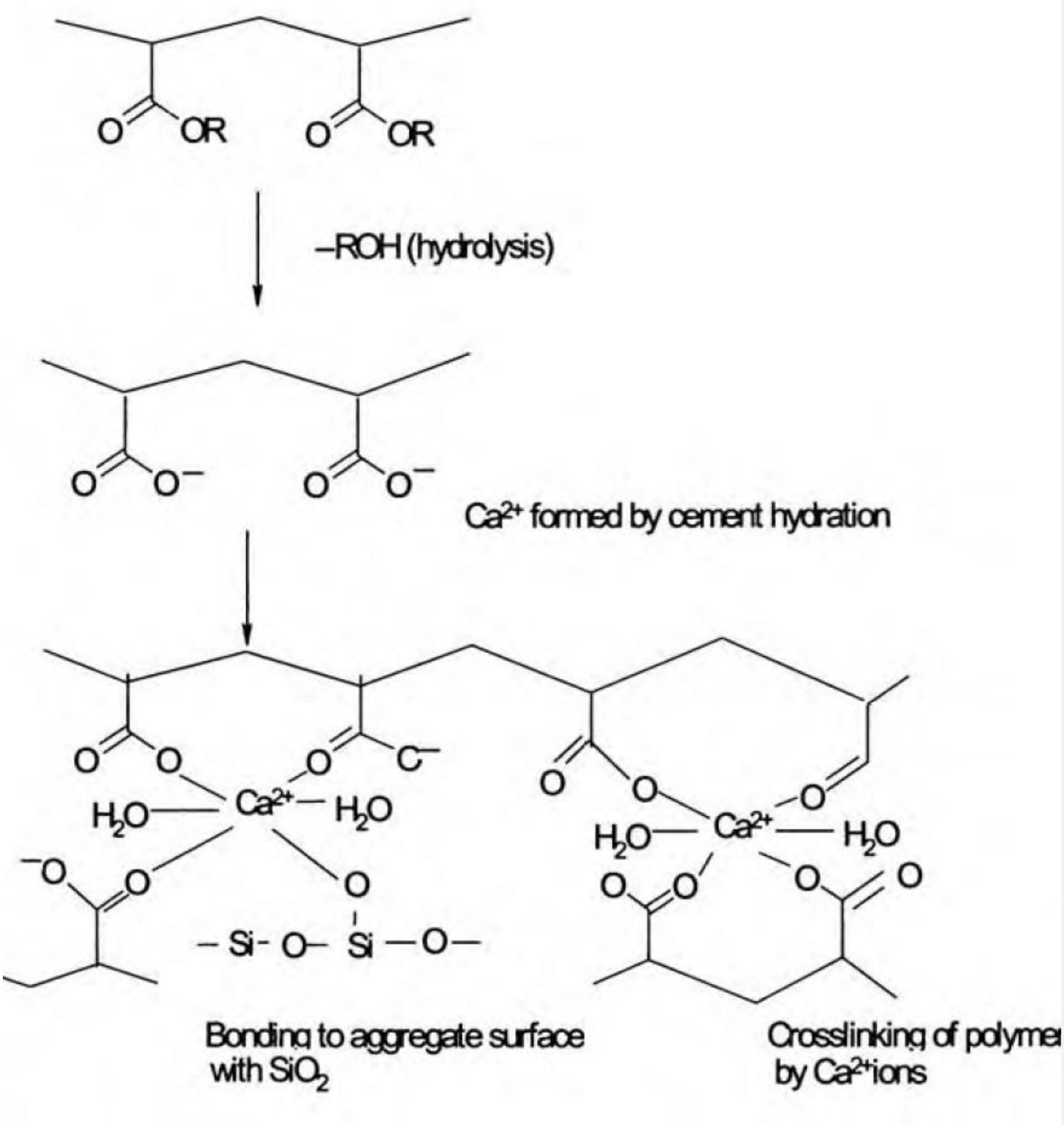


Figure 2.11 Schematic illustration of reaction between polymers with carboxylategroup (ester linkage) and ordinary Portland cement aggregate (Bing Chen & Juanyu Liu, 2007).

In the third step, the closely packed polymer particles coalesce to form a continuous film or membrane due to the withdrawal of *water* by cement hydration. This film forms a monolithic network in the polymer phase interpenetrating throughout the cement hydrate phase. The film formed by the latex acts as a bridge over the micro-cracks, thereby preventing crack formation and improves the cement hydrate and aggregate bond. This effect decreases the water wettability, resistance to moisture or air penetration, chemical resistance and improves with increasing *PlC* ratio (Bing Chen & Juanyu Liu, 2007).

2) ***Modification by redispersible powders****:* The principle of polymermodification by redispersible powders is almost similar to that by latexes. These redispersible powders are added to the cement in the dry state. They re-emulsify and behave similar to their respective latexes when water is added.

3) ***Modification by water-soluble polymers****:* Water-soluble polymers are added to the cement after dissolving them in water. This results in an increase in the viscosity of the water. The surface activity thus improves workability and prevents the "dry out" phenomenon. They form a thin film and contribute very little to the strength parameters of the composite.

4) ***Modification with liquid resins or monomers****:* The resins are added to the cement during the mixing at higher percentages than the latexes. Since the resins are of lower molecular weights or are prepolymers, further polymerization and cement hydration take place simultaneously. This results in an interpenetrating network of both the polymer and cement phases (Gominski et al., 2004).

2.9.3 Properties of PMC

Mortar is a mixture of sand, cement and water.

1) The polymer particles in the fresh mortar modified with polymer latexes exhibit a ball-bearing action, thereby improving its consistency. The *W/C* ratio is reduced with increase in the *PlC* ratio which contributes to strength development. Air entrainment is more than unconventional cement concrete. Therefore, the freeze-thaw durability and consistency are improved.

2) The setting process is dependent on the polymer type and *PlC* ratio and is generally delayed compared to the conventional mortars and concrete. The strength of these composites is influenced by various factors that tend to interact with each other. The main factors are (Ramakrishna & Sundararajan, 2005):

a. the nature of the materials used, i.e. the polymers, cements and aggregates;

b. the control factors for mix proportions such as *PlC* ratio, *W/C* ratio, binder-void ratio, air content etc.; and

c. curing and testing methods. Most of the PMCs and PMMs provide a larger ductility than ordinary cement concrete and mortar. PMC and PMM have a coefficient of thermal expansion equal to or slightly greater than ordinary cement concrete. The resistance to chloride ion penetration and carbonation is improved with increasing *PlC* ratio. The effects of filling and sealing by polymers are reflected in the reduced transmission of such gases as CO_2, O_2 and H_2O (vapour) as well as water impermeability. These also have excellent adhesion properties, high abrasion resistance and good chemical resistance superior to those of ordinary cement mortar and concrete (Ramakrishna & Sundararajan, 2005).

2.9.4 Applications PMC

PMC and PMM are being widely used as construction materials throughout the world due to the above cited advantages. In Japan research on polymer mortar and cement has been carried out for more than 40 years. Of late polymer-modified paste and slurry with high *PlC* ratios have been used as a liquid applied compound for waterproof membrane coatings for apartment, houses, silos and underground tanks in Japan and Germany (Ramakrishna & Sundararajan, 2005). Ethylenevinyl acetate is employed to improve workability and adhesion of fresh cement mortar. Water-soluble polymers such as methylcellulose, hydroxyl methylcellulose, polyvinyl alcohol and poly acrylates are used for plastering and underwater concreting work. Studies on the carbonation, chloride ion penetration, and oxygen diffusion characteristics reveal PMC as a low-cost, promising material to prevent corrosion of building structures. Some polymers like poly (vinylidene chloride-vinylchloride) release chloride ions, which cause corrosion of structural steel supports

Ethylene-vinyl acetate (EVA) is usually used to improve the workability and adhesion of fresh cement mortars. Commercially available epoxy resin (EP), unsaturated polyester (UP) resin (polyester-styrene system), vinyl ester resin (VE) and acrylic resin have been used to prepare PMCs (Mohr et al, 2005). The cure temperatures of poly methylmethacrylate mortars and concrete have been found to be far lower than that of ordinary cement concrete. Rods of fiber-reinforced plastics have been used to reinforce the structures with polymer mortars and concrete. Ohama (2006) recently developed an epoxy-modified mortar without any hardener that exhibits considerable strength below 20%. In Gennany, developments in epoxy modified mortars and concrete include a one-component epoxy resin for the cement modifier and a dry mortar using epoxy resin. The former does not require hardeners to be added at the construction site while the latter is produced as a dry mixture of epoxy resin with a hardener, cement and aggregates. The dry mixture can be applied by the addition of water in the field (Roma Jr et al., 2008).

Research on SBR-modified and unmodified lightweight aggregate concrete (LWAC) in Brazil revealed that the polymer increased the workability and cohesive nature of the mix in the fresh state. SBR- modified LWAC exhibited high structural efficiency compared to the unmodified one though its compressive strength is lower (Roma Jr et al., 2008). Hydroxyethyl cellulose (HEC) and EVA are added to anhydrous cement and aggregates. HEC has a major effect on the freshmortar properties such as water retention capacity and rheology. EVA influences the behaviour of hardened mortars.

Polyvinyl alcohol based polymer modified concrete and mortars showed that the polymer caused several changes in the micro structure. Some work done to overcome the problems due to re-emulsification of some copolymers like styrene butadiene, vinyl acetatc-ethylene, styrene-acrylic andacrylics revealed that a newly developed epoxy emulsion-based polymer exhibited better chemical and mechanical properties (Roma Jr et al, 2008). Bing Chen & Juanyu (2007) studied the effect of lightweight expanded polystyrene (EPS) on SBR latex modified concrete and compared it with the EPS concrete. The SBR latex improves the bond between the cement matrix and EPS particles at certain polymer cement ratio and increases the flexural strength.

2.10 Polymer Concrete

This was used as early as 1958 in USA, Japan and Soviet Union (Coutts, 1988) to produce building cladding and consisted of aggregates with a polymer binder without Portland cement or water. Polyester-styrene, acrylics, epoxies, vinyl and furan ester and urethanes are widely used. Since the polymeric binders replaced the conventional mortars and concrete, the polymer matrix binds the aggregates. Properties such as strength, chemical resistance, freeze-thaw resistance and abrasion resistance are better than those of conventional concrete or mortar. The poor resistance to high temperature and the dependence of the mechanical properties on temperature are the major undesirable properties of this group of polymer cement composites. Thermoplastics are serviceable till their glass transition temperature is above the level where they lose their mechanical properties. This could possibly be improved by employing crosslinking agents and thereby increasing the glass transition temperature. Thermosetting resins retain their properties till their decomposition temperature. Since the cost of various polymers is high compared to Portland cement and other cements, the mix design must ensure minimal percentage of polymeric binders to disperse aggregates under closely packed conditions in the polymer matrix.

2.10.1 Processing

Polymer concrete is prepared by using forced mixing type mixers. The proportions of the polymer binder range from 9-25% of the total mass. The mix proportions usually used are - Polymers: Fillers: Aggregates – 1:0-1.5:3-7.0. Fine aggregates used for PC are river gravels and sands and for coarse aggregates, crushed stones such as limestone, granite and silica sand etc. Fillers most often used are ground $CaCO_3$, powder or fumed silica and fly ash. After mixing, the PC mixtures can be cast or moulded in a manner similar to conventional cement concrete and then subjected to ambient temperature or heat cure. Trowels are often used for surface finishing. PC is very difficult to work on compared to conventional concrete with the exception of PMMA or acrylic mortars and mortars using low viscosity MMA I11 monomer. These harden faster than cement concrete thereby reducing the labour costs (Xu et al., 1996).

2.10.2 Properties

Since polymeric binders have poor thermal stability the properties are dependent on temperature. PC has a large hardening shrinkage and reaches about 5-10 times the drying shrinkage of ordinary concrete. They have good abrasion resistance, impact resistance and electrical insulating properties though they are mostly temperature dependent. PCs are completely monolithic and have a watertight microstructure with a chemical binder and filler. They are, thus, impermeable to chemicals, moisture and gas. Since they absorb no moisture, they are superior in terms of freeze-thaw resistance in most cases except for polyester resins (Toleˆdo Filho et al., 2000).

2.10.3 Applications

PC overlays have been in use as bridge surfaces and floors in sports arenas and stadia, laboratories, hospitals, factories and entrances. They are also used to manufacture drain pipes, underground boxes, man-hole covers, building cladding, floor tiles, architectural mouldings and machine tool bases. Though a considerable amount of research has been carried out on polymer concrete in the past three decades, its engineering properties have not been explored in depth. Vipulanandan (1990) have reportedly used organic polymers such as polyesters, epoxies and polymethylmethacrylates (PMMA) as binders for cement. His studies on polyesters and epoxies revealed that the strength, failure mode, failure strain and stress-strain rate are dependent on the curing method, strain rate and temperature. Fowler (1989) has studied methylmethacrylate PC and concluded that promoting ratios, testing temperature and aggregate type have varying effects on the strength of the composite. These effects may be possibly due to the thermoplastic nature of the polymer used. Vaidya and Nadkami (1987) have reported that recycled polyethylene terephthalate (PET) does not adversely affect the properties of the PC and therefore could decrease its cost. Wang Xin-You (1995) studied the fracture behaviour of the bonding interface between carboxylic styrene butadiene (SB) latex-modified cement mortar and old cement and found that the bonding strength increased with increasing amount of the polymer. The freezing resistance was found to be the best at *P/C=0.08* and is lower for ordinary cement mortar. Gominski et a1., (2004) assessed the storage modulus of PC using orthophthalic and isophthalic polyester binders and compared the results with Portland cement concrete. The results revealed that the type of the resin and concentration of fly ash used as filler had an effect on the modulus of elasticity of the composite. Pratap (2002) has studied the electrical applications of PC based on silica fillers (silica sand, desert sand, quartz powder etc.) with vinylester resin and acrylic resin respectively as binders, and concluded that acrylic-based PC is economical and has better electrical properties than vinylester-based PM.

2.10.4 Polymer Impregnated Concrete (PlC)

Polymer impregnated concrete and mortar are composite materials made by impregnating the hardened cement mortar and concrete with monomeric impregnates which are subsequently polymerized. Though this was developed in Japan, U.S.A and European countries during the 1960s and the 1970s, the high cost and complicated process technology involved made it increasingly unpopular (Chandra et al., 1994).

i) Principle

In this type of polymer cement composites the water or air filled pores in the hardened cement structures are fully or partially replaced by polymers. These composites have a microstructure in which the cement hydrate matrix phase, aggregate phase and the continuous polymer phase interpenetrate each other. As a result, the bonds between the cement paste and aggregates are stronger than those in the conventional ones. Consequently, these composites exhibit higher strength, chemical resistance and freeze-thaw resistance. The properties of a typical PlC (Chandra et al., 1994) depends mostly on:

1. Impregnation efficiency of the monomers;
2. Degree of conversion of the monomers into polymer;
3. Polymer impregnation depth and polymer loading; and
4. The properties of the polymers used.

ii) Materials

The materials used for PlC consist of monomeric impregnants, basemortar and concrete. The polymers most widely used in the impregnation of concrete are vinyl types such as methyl methacrylate, styrene, acrylonitrile, tertbutyl styrene and vinyl acetate. MMA and its mixtures with acrylonitrile are preferred due to their low viscosity, good wettability, high reactivity, relatively low cost and superior properties of the resulting composite. These polymers could be crosslinked with suitable agents such as trimethylolpropanetrimethacrylate to form a three dimensional network in the pores, thereby resulting in enhanced chemical and mechanical properties of the polymer cement composites. Thermosetting resins are very viscous. Hence less impregnation is possible though they increase the resistance of the composites to heat (Chandra et al., 1994).

iii) Processing

PlC is made by impregnation of precast hardened Portland cement concrete with low viscosity monomers (in either liquid or gaseous form) that are converted to solid polymer under the influence of physical agents (ultraviolet radiation or heat) or chemical agents (catalysts) (Chandra et al., 1994). It is produced by drying conventional concrete, displacing the air from the open pores (by vacuum or monomer displacement and pressure), saturating the open pore structure by diffusion of low viscosity monomers or a prepolymer-monomer mixture (viscosity 10 cps; I x 10-2 Pa's) and in situ polymerization of the monomer or

Comment [Kingsley6]: Check.

prepolymer-monomer mixture, using the most economical and convenient method (radiation, heat or chemical initiation). The important feature of this material is that a large proportion of the void volume is filled with polymer, which forms a continuous reinforcing network. The concrete structure may be impregnated to varying depths or in the surface layer only, depending on whether increased strength and/or durability are sought.

iv) Properties

The properties of the PlC depend on the polymer loading or polymer penetration depth. The main properties of a PlC (Chandra et al., 1994) are:

1. High strength similar to PC and PM;
2. Excellent water tightness and freeze-thaw durability;
3. Good chemical resistance depending on the degree of polymerpenetration;
4. Excellent abrasion resistance and impact resistance; and
5. Poor thermal resistance and fire resistance.

v) Applications

Applications include structural floors, high performance structures, food processing buildings, sewer pipes, storage tanks for seawater, desalination plants and distilled water plants, marine structures, wall panels, tunnel liners, prefabricated tunnel sections and swimming pool walls. Partially impregnated concrete is used for the protection of bridges and concrete structures against deterioration and repair of deteriorated building structures such as ceiling slabs, underground garage decks and bridge decks (Ohama, 2006).

Though composites of polymers show improved properties when low viscosity monomers are impregnated in hardened concrete, PlC is very expensive due to the high cost of the monomers. This is one of the main reasons why research and applications in this area are limited. Studies carried out on PlC using acrylic acid monomer (Gad et al., 1995), with different W*IC* ratios and cured for various durations indicated that the intrusion of polymer into the cement paste matrix does not affect the phase composition of the hydrated phases. It also revealed the dependence of the compressive strength on the initial W/C ratio, curing time and gel/space ratio. The properties of PlC are dependent on the glass transition temperature of the polymers or the copolymers used (Gad et al., 1995). Also the addition of crosslinking agents increases the strength at high temperatures. Investigations on the impregnation of surface of Highway Bridge decks with polymers revealed that it increased the durability and more study is underway (Neelamegam & Subrahrnanyam, 2006) to develop a practical method of application and evaluation of different treatments by various testing procedures.

2.10.5 Interactions When Polymers Are Impregnated in Concrete

In this case, the effective polymer loading is about 1.5-7.5%, which is much smaller when compared to that used in polymer cement concrete (which is about 15%). This lower effective loading is due to the fact that the impregnation of the polymer takes place after the hardening of the cement and there is no possibility of any interaction between the two phases. The polymer fills the voids and bridges the microcracks of the cement concrete structure and strengthens the concrete. The strength of the PlC is therefore due to the cumulative strength of the concrete as a whole and the adhesive bond provided by the polymer (Cheng-Hsin et al., 2006).

2.10.6 Interactions When Polymers Latexes Mixed in Concrete

Ideally when the polymer is mixed with the cement *concrete*, the latex does not undergo interactions with the cement and forms a film over the cement particles and bridges the microcracks while drying. In actual practice when the polymers are mixed with cement concrete there are reactions between the two phases which results in the coagulation of the latex**.** Thus, the latex loses its film-forming ability and this coagulation interferes with the normal hydration of the cement. This formation of complexes may results in acceleration or retardation of the cement hydration.When water is added to the cement, $Ca(OH)_2$ is released into the water. In the case of cement modified by acrylic polymers there is a reaction between theCa^{2+}, ions in the water and carboxylate ions present in the polymer. Chemical analysis of the pore solution indicated a comparable amount of OH ions in it (Su & Zao, 1995). XRD and thermal analysis of the cement pastes modified by acrylic polymers indicate a decrease in the amount of Ca^{2+}, ions and an increased amount of SO_4^{2+} compared to the unmodified cement paste. The relevant reaction takes place in two stages - first an attack on the carboxylate group (ester linkage) of the polymer by the hydroxide ions, known as saponification (or alkaline hydrolysis) followed by a reaction of Ca^{2+} ions with the carboxylic group (Su & Zao, 1995) as depicted in Fig.2.11.

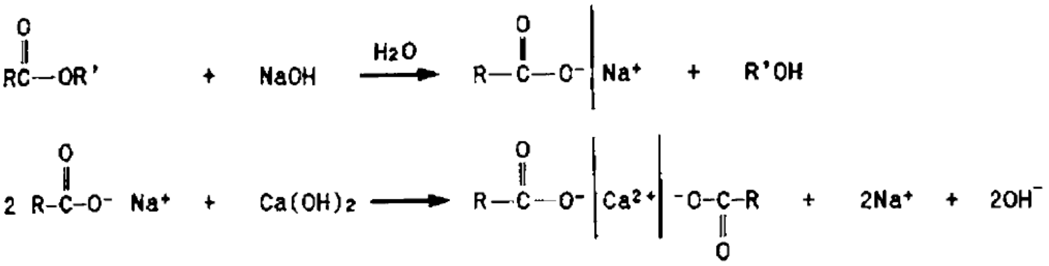


Figure 2.12: Alkaline hydrolysis of the acrylic polymers (Su and Zao, 1995)

Ohama (2006) suggested that the reaction between the Ca^{2+} ions and the carboxylic group could either result in chemical bonding between the aggregate surface and the $Ca(OH)_2$ group or in crosslinking of polymer chains by the Ca^{2+} ions as depicted in Fig.2.11. Investigations into the possibility of a polymer (styrene acrylate) film in the presence of $Ca(OH)_2$ revealed that there is a decrease in the extent of formation as the level of the $Ca(OH)_2$ increased. When the *PlC* ratio is less than 1:4 the polymer adheres on to the $Ca(OH)_2$ particle and loses its film-forming capacity (Gominski et al., 2004).

This phenomenon is not observed in the presence of NaOH. Therefore the interaction between the two phases results in an ionic bonding between Ca^{2+} ions and the carboxylate ions of the polymer-forming crosslinks which also inhibit film formation. This indicates further that the polymer latex does not undergo destabilization due to the alkalinity of the solution. The interaction between the reactive parts of the polymer and the Ca^{2+}ions has been under study by many research groups (Gominski et al., 2004). The analysis of the pore solution and the amount of Ca^{2+} ions in the modified and unmodified cement concrete revealed a different mechanism in the presence of polymer chains. The influence of this chemical interaction on the final properties has however not been investigated. Though the polymer particles or film influences the microstructure of the hydration products, the final structure depends on the polymer and *PlC* ratio. It has been observed that a continuous film formation is not possible if the percentage of polymer is less than 5% and behaves as an additive (Gominski et al., 2004). Depending on its type the polymer deposits, as droplets, on the surface of the hydrated and unhydrated cement particles and coalesces to form a film. In this way the polymer partially or completely hinders the hydration of cement particles. Therefore, the structures of the bulk binder phase of the modified and unmodified phases differ in the degree of crystallinity and the morphology of the $Ca(OH)_2$. In the unmodified cement, the formation of crystals of $Ca(OH)_2$ is distorted and accommodated to spaces formed by the structure of the unhydrated particles and the primary hydration products. However the formation of $Ca(OH)_2$ crystals in the presence of polymers takes place without any deformation (Su et al., 1991). Therefore the polymer acts as a bonding agent trying to bridge the different layers, thereby increasing the interparticle bonding. The existence of chemical bonds, however, cannot be concluded from structural investigations. Su et al., (1991) found that $Ca(OH)_2$ crystals are formed at the interface between the cement hydrates and limestone or aggregates in the presence of the polymerlatexes.

2.10.7 Models of Polymer Modification

Many authors have proposed theories on the formation of the microstructure of polymer mortar and concrete (Su et al., 1991; Bijen & Su, 1995; Ohama, 2006). They have explained the structure of the matrix consisting of the interpenetrating polymer phase and hydrated cement with random dispersion of the aggregates. SEM studies revealed the presence of the polymer film in capillary pores, bridging opposite sides of propagation cracks and around the aggregates. Ohama (2006) proposed the basic model of polymer modification of cement concrete and many refinements were proposed. Though the models gave a good idea about the micro and macro structures, the chemical interactions between the two phases still remain uncertain.

Comment [Kingsley7]: Full meaning?

i) A three-step model proposed by Ohama (2006).

ii) Modification of the three-step model proposed by Bijen & Su (1995)

This theory was based on observations made on an Environmental Scanning Electron Microscope and suggested some refinements and additions to Ohama's model (2006). In the first step, it is assumed that there is equilibrium between the polymer particles in the liquid phase and the adsorbed polymer particles on the cement surface. This depends on the type of the polymer and cement, dispersing agents in the polymer and the *PlC* ratio. The efficiency of the polymer modification is more when there are fewer polymer molecules adsorbed on the cement particles. This is so because they hinder the movement of the capillary water to the unhydrated cement. This slows the hydration process of the cement and is observed in the case of many polymers.

Comment [Kingsley8]: The word here was ‘adsorbed’

Comment [Kingsley9]:

As the degree of hydration proceeds with water consumption, the layer of adsorbed polymer molecules also thickens. Therefore, it takes a long time for the cement products to penetrate the polymer layer. The morphology of the cement hydration products in the pore regions is more crystalline and is influenced by the polymers dispersed in the liquid phase.

Comment [Kingsley10]:

Plate and needle shaped products are formed in the pore regions and consist of inorganic and organic polymeric materials. At this stage the polymer forms bridges between different particles. As the formation of the cement hydration products takes place the amount of free available water is restricted to areas where capillary pores are in the unmodified state.

Depending on the minimum film-forming temperature, the amount of the polymer and the existing temperature, the polymer molecules coalesce to form a film. When the *PlC* ratio increases the film is continuous and forms an interlinked, uniformly distributed skeleton in between the cement hydrate layers (Putennan & Malomy, 1998). With lesser percentage of polymer molecules, they get distributed evenly with or without mutual contacts. A minimum of 5% of the polymer is essential for continuous film formation. Above 9% of polymer in the whole volume *(PlC* = 6.4%. with sp.wt of cement= 3.01 kg/m] and polymer emulsion=1 kg/m] and 350 kg cement) a continuous phase is formed which is intimately mixed with the cement hydrate phase. Above 18% *(PlC* - 14%) the two phases still exist with a polymer phase free of cement hydrates which result in increased in ductility, in compression as well as in tension.

iii) Modification of three-step model by Puterman and Malorny (1998). This theory was propounded by studying the interactions of the polymer dispersion and cement particles at the early stages of hydration using SEM. In the second stage, the closely packed polymer particles coalesce to form a film provided that its minimum film temperature (MFT) is lower than the hydration temperature. MFT is the minimum temperature during which the polymer particles coalesce to form a film. The cement hydration takes place where the cement particles have access to free water. An external layer of hydrated products is formed on some parts of the cement grains which results in some of the cement particles remaining unhydrated. As the hydration goes to the final stage, the cement particles grow into products that sometimes penetrate the polymer film. The particles connect to each other incorporating the polymer film around and within the cement gel particles. Investigations on the polymer film on the cement surfaces by Larbiand Bijen (1990) revealed that the cement particles penetrated it during the hydration process. Therefore, the polymer film does not contribute to the properties though, however, it improves the workability and hydration rate during the start of the cement hydration.

The *PlC* ratio is a major factor in determining the ability of cement hydration products to penetrate the polymer film and to finally access the freewater and complete the hydration (Larbiand Bijen, 1990). When the *PlC* is lower than 16%, the penetration of the film by the cement particles takes place. At higher percentages, the polymer forms an impermeable membrane around the partially hydrated cement particles which have no access to free water. This theory lays emphasis on the minimum film formation temperature (MFT) of the polymer used in the polymer cement composite. If the MFT of the polymer is above the curing temperature of the cement, the polymer remains as a thick layer of stacked droplets on the surface and does not form a film. This layer is permeable and may improve the properties and toughness of the composite.

2.11 Current Status of Polymer Cement Composites

Lately significant work on the development and application of new polymer cement composites have been carried out (Larbiand Bijen, 1990). These composites are mostly used as repair and construction materials and possess excellent mechanical and durability related properties. After the oil crisis in 1970's it was clear that mineral oil was no longer available as the cheap basis for polymer production. The use of polymers in construction industry, therefore, became limited, and focused on scenarios where high durability and sustainability were considered important. Polymers are thus currently used in areas where their specific properties are required to contribute to a synergistic effect with the classical construction materials (Priya Viswanath et al., 2005).

Comment [Kingsley11]: In Nigeria, or all over the world?

Polymers are added either to the fresh concrete mix or to the hardened Portland cement concrete in the form of a complete polymer (premix polymerised latexes - elastomers or thermoplastics) or chemically reactive synthetic resins - prepolymers or monomers that may be polymerised or polycondensed (post-mix polymerised) by thermocatalytic or other systems. Some of the premix polymers used are polyacrylic esters, styrene butadiene rubber, polyvinyl alcohol and copolymers of styrene with acrylic esters and butadiene. Epoxy resins are widely used as a post-mixpolymer. In Japan, research and development in the field of polymer modified mortar and concrete have been carried out for several years. These are used mostly for their high performance, multi-functional applicability and sustainability compared to conventional cement concrete or mortar. Styrenebutadiene rubber (SBR) latex, polyethylene vinyl acetate (EVA) and polyacrylic esters emulsions are some of the dispersions used. Commonly used resdispersible powders include poly (vinyl acetate- vinyl versatate) and EVA. PMM is mostly used for repair and finish works (Priya Viswanath et al., 2005) but PMC has limited applications.

In Korea, polymer cement concrete is mainly used for bridge overlay while polymer cement mortar is used for repairing buildings, bridges and concrete pavements (Priya Viswanath et al., 2005). Polymer concrete and mortars are employed in the manufacture of manhole covers, cable troughs and reinforced plastic composite pipes. The use of MMA modified UP polymer concrete and mortar in bridge decks, sewage manholes and oceanic pile are also being studied. PICs are mostly used for job site impregnation and have very limited applications due to their high cost. Most of the polymers used as construction admixtures are SBR, PAE, waste polyethylene terephthalate. Waterproofing is done with cement blended rubber latexes like synthetic rubber, natural rubber and rubber asphalt.

In China, the use of polymer modified mortars, including latex modified mortars and mortars modified with redispersible powders in various civil applications are being investigated. The main PMC based products are tile adhesives, concrete interface treatments, adhesives and surface-protecting mortars, polystyrene foam boards for thermal insulation of buildings and water proofing materials. Polymer concrete and polymermodified mortar and concrete are mostly used for repair of roads, dams and buildings. Some of the polymers used are SBR, specially developed carboxylic butadiene/styrene copolymer (for oil well consolidation), copolymer of vinyl acetate with methacryloxyethyl trimethylammoniumchloride and steel fibre reinforced concrete.

In India, around 6% of polymeric materials have been used in construction and in the production of pipes, gutters, window and door profiles, insulation, bridges and building panels. Polymer-modified mortar and concrete are used as repair materials and investigations have revealed that steel fibre reinforced natural rubber latex concrete have superior durability and ductility (Priya Viswanath et al., 2005). SBR and polyacrylic rubber latex modified concrete with and without the use of steel fibre with normal aggregate viz. sintered fly ash aggregate are being developed. The latex modified RC beams showed increased initial crack load and improved load deflection behaviour. Epoxy and polyester resins are now employed in polymer cement and concrete and are applied as repair materials in airfields, cement concrete highway pavements and dumper platforms for iron ore handling plants. The resins used as binders for cement are MMA and polyester. Fibre-reinforced polymer composites are also used in the RC plates and laminates.

In Europe, the use of polymers have gradually extended from concrete crack injection to repair mortars for concrete and stone, consolidation of masonry, repair of timber structures, piping and waterproofing materials. On a relative average of 8% for the polymer consumption concerns thermosets, the rest being thermoplastics. In 2003, 7350000 tons or 18.5% of the total market of polymers in Western Europe (European Union, Norway and Switzerland) were used in building and construction industry (Priya Viswanath et al., 2005).

2.12 Mechanics of Fibre Reinforcement of Cement Materials

The primary aim of incorporating fibres in cement matrix is to increase its resistance to crack propagation, thereby increasing its relatively low tensile and flexural strength which is attributed to the ability of the fibres to resist crack growth. The mechanism of crack arrest can be qualitatively explained using Figure 2.12.

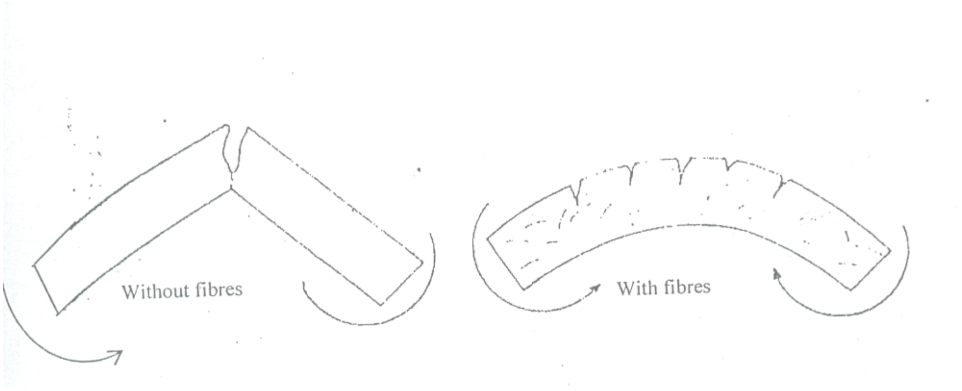


Figure 2.13: Crack Arrest in Fibre

Without the fibres, the crack runs through the material very easily as the brittle cement has very small value of fracture energy and so has minimal resistance to crack growth. When fibres are present and the failure strain of the fibres is much greater than the cracking strain of the cement, then the fibres remain in place bridging the crack. If the fibres are sufficiently strong, the piece will remain unbroken because the fibres hold it together. On continued straining, the weak matrix will break again at another place and will be held together by the fibres bridging the cracks (Eze-Uzomaka & Nwadiuto, 1990). The efficiency of this crack arrest mechanism is therefore dependent on the strength and amount of fibres present. As a result, the properties of the fibres-reinforced cement composite are dependent on a number of factors. These include fibre geometry, fibre spacing, fibre volume percent and aspect ratio, fibre orientation and mix proportions.

2.12.1 Fibre Geometry

The failure of fibre-reinforced cement is usually due to fibre pull-out, and improving the mechanical anchorage of the fibre was found to be more important than any chemical treatment of the fibres. This can be achieved most easily with metallic fibres during the cutting process. The performance of such fibres when used to reinforce cement paste beams has been reported to be excellent (Eze-Uzomaka & Nwadiuto, 1990).

2.12.2 Fibre spacing

The strength of concrete or mortar with an inherent internal flaw structure can be increased by decreasing the size of the flaws. This approach was taken by Chung and Pu-Woei Chen (1993) to increase the tensile strength of concrete using closely spaced wires as crack arrestors. They showed theoretically and experimentally that the stress required to extend a crack beyond the area enclosed by adjacent groups of fibres is inversely proportional to the square root of the fibre spacing, and thus proposed an expression for predicting the first crack strength of fibre-reinforced concrete. It was suggested that the effect of the fibre on the tensile strength of concrete becomes quite significant at fibre spacing below about 12.7mm even when the fibres are short and randomly oriented. However, comparison of experimental results of other researchers tends to show that the spacing concept does not accurately predict the first crack strength of fibre-reinforced concrete.

2.12.3 Fibre Volume Percent and Aspect Ratio

Generally the two most important factors which influence the maximum load of fibre-reinforced mortar are the volume percent of fibres and their aspect ratio. Furthermore, it has been shown that if segregation of fibres is avoided, then increasing volume percent of fibres more or less linearly increases the strength of the composite. Similarly, it has been shown that up to the aspect ratio of 150, increasing the aspect ratio linearly increases the maximum load. Based on these observations, the ultimate strength of the composite is given by (Eze-Uzomaka & Nwadiuto, 1990):

$$S_c \ - AS_m \ = V_f \ + BV_f \ (L)d \qquad (2.2)$$

where S_c and S_m are the ultimate strengths of the composite (fibre reinforced concrete) and the matrix (mortar or concrete) respectively. L denotes the length of the fibres and d is the diameter of the fibre. A and B are constants which can be determined by a plot of composite strength against $V_f L/d$. Note that A is dimensionless and B has the same units as those of S_c and S_m.

2.12.4 Fibre Orientation

Maximum composite strength occurs when all the fibres are aligned parallel to a uniaxial tensile load. As a result, the strength of fibre-reinforced cement is dependent on the degree of alignment of the fibres in the direction of the load. Alignment of steel fibres, done by applying a magnetic field and vibrating the specimen while it is still plastic yields pronounced increases in flexural strength over randomly oriented fibres. A flexural strength for aligned fibres of 26.0 MPa was reported for 1.2 percent by volume of deformed steel fibres compared to 9.0 MPa for the same type and amount of fibres randomly oriented.

The efficiency of the fibres can also be improved by compacting specimens by table vibration, which tends to produce an orientation of fibres in two or three dimensions depending upon the size of the aggregate and the dimensions and concentration of the fibres (Yunping et al., 2004). This orientation occurs because the fibres tend to rotate until they are at right-angles to the direction of gravity or to vertical acceleration.

2.13 Mechanical Properties of Cement Mortar

In structural design, the first consideration is for the structural elements to be able to carry the loads imposed; therefore strength is considered to be the single most important mechanical property of concrete. Strength is also an essential property because it is related to several other essential properties which are more difficult to measure directly, and a simple strength test can give an indication of these properties; for example, increase in compressive strength of concrete gives an increase in modulus of elasticity. The strength of cement mortar has to be qualified with terms such as tensile strength, flexural strength or compressive strength (Newman & Choo, 2003).

The compressive strength of the material is generally specified because the working stress theory for concrete design considers concrete as generally appropriate for sustaining compressive load. The tensile and flexural strengths of concrete are typically of the order of 10 and 15 percent respectively, of the compressive strength. Such a large difference between the tensile and compressive strength is attributed to lack of elasticity, heterogeneousness and complexity of the micro-structure of cement mortar (Materials Research, 2005). Strength of cement mortar may be measured in a number of ways, such as strength in compression, in tension, in shear or in flexure. All these indicate strength with resistance to a particular method of testing.

2.13.1 Compressive Strength and the Need for Compressive Test

Strength is the property normally specified in cement mortar design and quality control. This is because other properties of cement mortar, such as elastic modulus, water tightness or impermeability, and resistance to weathering agents including aggressive waters, are understood to be reliant on strength and may therefore be deduced from the strength data. The compressive strength of cement mortar is several times higher than other types of strength; therefore a majority of cement mortar elements are designed to take advantage of the greater compressive strength of the material. The variables that have an effect on the strength of cement mortar are shown in Figure 2.13.

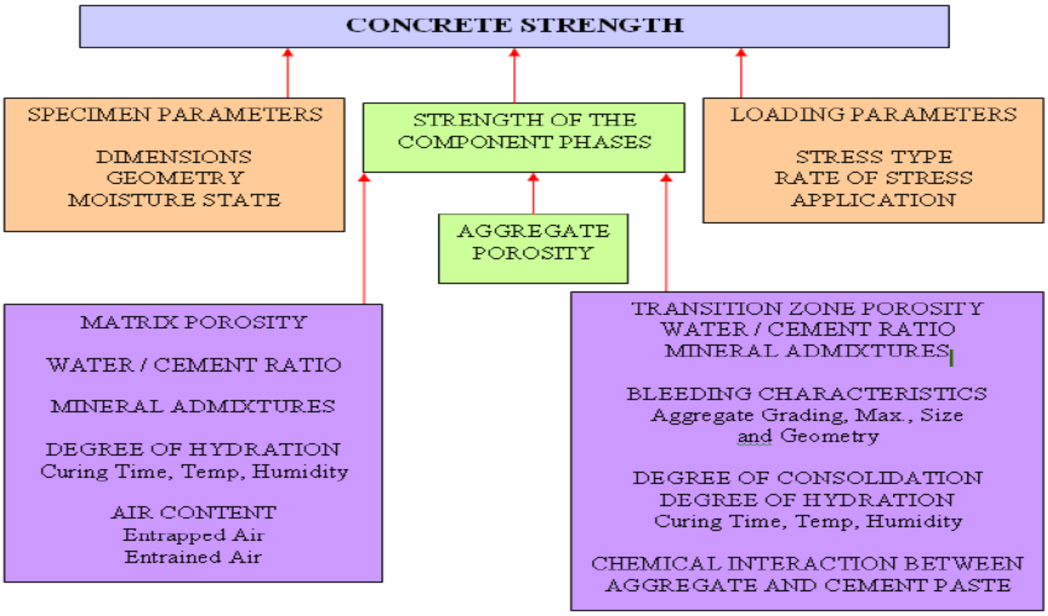


Figure 2.14: Factors influencing concrete strength [adopted from Crane and Charles, 1997].

Compressive strength is usually defined as the measured maximum resistance of a concrete or mortar specimen to axial loading. It is normally expressed in Mega-Pascals (MPa) at an age of 28 days and is usually specified by the symbol fc. Compressive strength can be used as an index to judge flexural strength, once the relationship has been established for the particular mix design and size of the unit (Crane & Charles, 1997).

2.13.2 Flexural Test

Direct testing of cement mortar under tension is not possible because of its brittleness since it is difficult to grip and align. Eccentric loading and failure at or in the grips is very hard to avoid. Therefore, the flexural test is preferred. This provides a way of measuring the material’s behaviour subjected to beam loading. Flexural strength is the ability of a beam or slab to resist failure in bending. The flexural strength is usually expressed as Modulus of Rupture (MR) in MPa. Hence, laboratory mix design based on flexure may be necessary, or cement content may be chosen from past experience to yield the required design of MR. MR can be employed for field control and in the acceptance of pavements. Flexural testing is used on a very few occasions for structural concrete (Crane & Charles, 1997).

2.13.3 Fracture of Cement Mortar

Even though cement mortar is a primitive and most commonly used material, a lot of properties and characteristics of cement mortar are neither easily nor accurately understood, and research is still being continued using various techniques to acquire better knowledge of the characteristics of cement mortar. Due to its main uses in building and construction works, as well as a selection of other heavily used applications (e.g. roadwork), understanding of its mechanical behaviour is receiving attention from engineers and scientists using a variety of testing methods; but owing to its complex nature, there are issues of concern to both the manufacturers and users. Cement mortar behaves like a structure of two dissimilar materials (aggregate and cement paste) which becomes more complex by the various quantities of materials that either make up the cement paste or function as the aggregate. The interface between the aggregate and cement is usually considered as the weakest link (Jan & Mier, 1997) in cement mortar which consequently has a major effect on the mechanical behaviour of cement mortar.

The interfacial bonding between the cement and aggregate performs a crucial function in the strength of concrete. With the hardening of fresh cement mortar, loss of moisture starts occurring in the cement paste causing shrinkage. Shrinkage does not occur in the aggregate material; the boundary conditions of the structure or the object during casting resist the shrinkage of the cement paste. The boundary conditions, non-uniform distribution of shrinkage strain and the restraints from the aggregates cause increase to tensile stresses. These tensile stresses give rise to internal flaws and cracks within the concrete before the application of any external load (Crane & Charles, 1997). The mechanical behaviour of concrete is controlled by the existence and propagation of these internal cracks during loading.

It is difficult to observe the fracture nature of concrete because of its complexity. This makes the crack propagation in concrete complex and it chooses a path based on the structure and constituents of the material, hence its behaviour is not predictable. The design of concrete structures, according to Adachi et al., (2002), is becoming increasingly necessary to look at crack growth and propagation to avoid catastrophic failure. Failure in concrete is usually due to crack propagation. Understanding the reasons and the circumstances under which concrete fails are important for design of concrete structures, as well as developing new cement-based materials.

When it is difficult for cracks to grow, a material is said to be tough and when crack propagation is easy, it is known as a brittle material. It would therefore clearly be useful to have a technique that is able to detect a crack and its propagation (Crane & Charles, 1997). A number of techniques exist that are categorised as non-destructive testing techniques, which are designed to detect, and usually size, stationary cracks without damaging the serviceability of the component. However one technique exists and is readily available, which can detect a growing crack but not an inactive crack; this passive technique is called acoustic emission (AE). It is the application of this AE technique which is considered in this work.

2.13.4 Microstructure of Concrete

Many characteristics of concrete do not abide by the laws of mixture even though it is a composite material. For example, if both the aggregate and the hydrated cement paste under compressive loading are separately tested, it would fail elastically, whereas concrete itself exhibits inelastic behaviour prior to fracture. In addition, the strength of concrete is normally much lower than the individual strength of the two components. These irregularities in the behaviour of concrete can be justified on the basis of its microstructure, particularly the vital function of the interfacial transition zone between coarse aggregate and cement paste (Akpabio et al., 2012).

It is essential to understand the microstructure of concrete to understand the crack propagation in concrete. It is very difficult to establish a clear pattern of the microstructure of concrete from which an opinion of the material’s behaviour can be formed with confidence since concrete has a highly heterogeneous and complex microstructure. The developments in the area of materials have resulted mainly from recognition of the principle that the properties originate from the internal microstructure, i.e. modification can be made to the properties of materials by making appropriate alteration in the microstructure of a material.

The distinctive features of the concrete microstructure are (Crane & Charles, 1997):

i) Interfacial Transition Zone, representing a small region next to the particles of coarse aggregate. It exercises a far greater influence on the mechanical behaviour of concrete than is reflected by its size.

ii) Each of the three phases is itself a multiphase in character. For example, each aggregate particle may contain several minerals in addition to micro-cracks and voids;

iii) The microstructure of concrete is not an intrinsic characteristic of the material, because the two components of the microstructure (interfacial transition zone and hydrated cement paste) are subject to change with time, environmental humidity and temperature. The theoretical microstructure-property relation models are not much helpful for predicting the behaviour of concrete mainly because of the highly heterogeneous and dynamic nature of the microstructure of concrete. To understand and control the composite material such as concrete, a broad knowledge of the important features of the microstructure of each of the three phases of concrete is nevertheless important (Crane & Charles, 1997).

2.13.5 Toughening Mechanism in Concrete

The toughness is a measure of energy while the strength is a measure of the stress required to fracture the material. Thus two materials may have very similar value of strength but different toughness values. With the propagation of cracks in concrete, many toughening mechanisms start taking place. The inelastic zone around a crack tip is expressed as the fracture process zone and is the location of these toughening mechanisms. Crack shielding, crack deflection, aggregate bridging, crack tip blunting and crack branching are some of the most common toughening mechanisms known until the present moment (Crane & Charles, 1997).

Crack shielding takes place when the major crack propagates into a zone that consists of a high density of flaws, such as water-filled pores, air voids attained during casting process and shrinkage cracks. Part of the energy being introduced by the applied load is consumed by the high-density flawed region. Compared to the main crack, the flawed region has a random orientation and therefore does not make contribution to the propagation of the main crack. When the main crack must alter its direction of propagation due to a strong particle, such as an aggregate lying in its path, crack deflection occurs. If the main crack path is altered more, then the greater amount of energy must be introduced into the material to cause fracture. When a crack has advanced beyond and through a particle, such as an aggregate, which is capable of distributing stresses from one side to the other (of the main crack), bridging occurs. This transfer of stress is continued until the particle ruptures or is pulled out. Bridging is at times purposely introduced (glass slide in this investigation) into concrete by adding small fibres to serve as bridges across the surface of the cracks. Some of the commonly used fibres are steel, polypropylene, aramide and glass fibres (Crane & Charles, 1997). The propagation of the main crack is occasionally terminated by a large internal void; this toughening mechanism is termed crack tip blunting. When a crack tip propagates into a void, the tip of the crack becomes blunt and an extra amount of energy is needed to propagate the crack with a blunt tip. When the main crack splits into two cracks, the toughening mechanism of crack branching is introduced into the specimen. More energy is needed to propagate two cracks through concrete than it does to propagate one crack.

These toughening mechanisms take place amongst one another and absorb a part of the energy being introduced into a concrete specimen by an external force or movement. The fracture mode of a cementitious material relates very closely to the nature of fracture process that takes place in that material, based on the understanding of the conditions under which a number of toughening mechanisms can occur in a given material, it may be possible to control the fracture mode by tailoring the material microstructure (Crane & Charles, 1997).

2.14 Thermal Decomposition of Natural Reinforcement in Cement Mortar

Previous research in thermal decomposition of natural reinforced composites was primarily motivated by applications such as renewable biomass energy and natural fuels (Malek et al., 2001). Due to the complexity of thermal decomposition reactions of natural reinforced composites, extensive research has been done in determining individual behaviors of the main components (or pseudo- components) of natural reinforcers (e.g., pure cellulose, lignin, and hemicelluloses). For practical engineering applications, however, it may be sufficient to consider only the basic characteristics of the thermal decomposition process with some simplified mechanisms (Gronli et al., 2002).

For naturally reinforced cement composite processing, it is of more practical relevance to understand and predict the thermal decomposition of the reinforcing based on the simplified kinetic scheme and parameters under specific process temperature of natural reinforcer composite. However, there have been few fundamental studies in this field. Moreover, the reported values of kinetic parameters for natural reinforcer were in a large range, e.g., activation energy for pure cellulose from 100 and 250*kJ*/*mol (*Malek, 1992).

This variability was primarily caused by different kinetic schemes used and pre-assumption of the reaction function and reaction order in kinetic modeling process. The suitable kinetic models for natural fibers remain to be developed (Malek, 1992). A method proposed by Málek and his co-workers allows fairly reliable kinetic analysis and interpretation of non-isothermal TG-DTG data (Malek, 1992; Malek et al., 2001).

2.14.1 Theoretical Approach of Thermal Decomposition

The fundamental rate equation used in all kinetic studies is generally described as (Malek et al. 2001):

$$d\alpha / dt = kf(\alpha) \qquad (2.3)$$

Where k is the rate constant and *k*, *f*(α) is the reaction model, a function depending on the actual reaction mechanism. Eq. (2.3) expresses the rate of conversion, *d*α/*dt*, at a constant temperature as a function of the reactant concentration loss and rate constant. In this study, the conversion rate α is defined as (Liu and Fan, 1998):

Comment [Kingsley12]: Something is missing here.

$$\alpha = (W_0 - W_t)/(W_0 - W_f) \qquad (2.4)$$

where *W*0, *Wf and Wt* are time, initial and final weights of the sample respectively, the rate constant *k* is generally given by the Arrhenius equation (Liu & Fan, 1998):

$$k = A\exp(-E/RT) \tag{2.5}$$

where *E* is the apparent activation energy(Kj/mol) , R is the gas constant (8.314J/K.mol), *A* is the pre-exponential factor (s^{-1}), T is the absolute temperature (*K*). The combination of Eqs. (2.3) and (2.5) gives the following relationship (Liu and Fan, 1998):

$$d\alpha/dt = A\exp(-E/RT)f(\alpha) \tag{2.6}$$

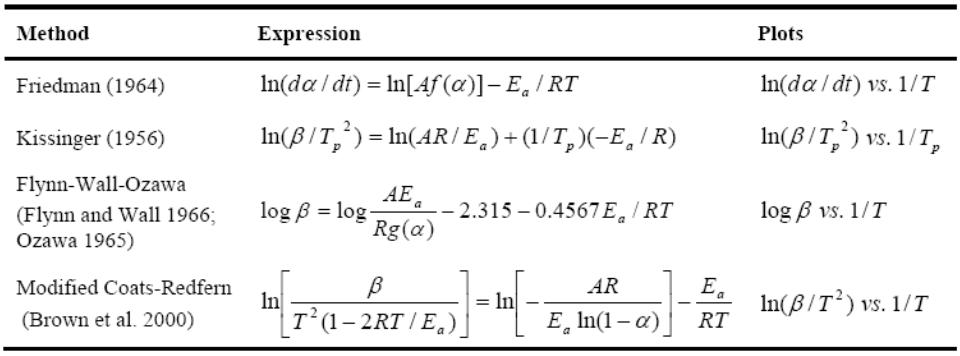
For a dynamic TGA process, introducing the heating rate, β= *Dt/dt* into Eq. (2.6), Eq. (2.7) is obtained

$$d\alpha/dT = (A/\beta)\exp(-E/RT)f(\alpha) \tag{2.7}$$

Eqs.(2.6) and (2.7) are the fundamental expressions of analytical methods to calculate kinetic parameters on the basis of TGA data. The most common “model-free” methods used in this study are summarized in Table 2.4. The Friedman method is the isoconversional method, which directly leads to -*Ea*/R for a given value of α by plotting the term ln(*dα*/*dt)* against 1/T. In the Kissinger method, is in (β/T^2_p) plotted against $1/T_p$ for a series of experiments at different heating rates with the peak temperature, T_p, obtained from the DTA curve.

The isoconversional Flynn-Wall-Ozawa (F-W-O) method is the integral method, which leads to -*Ea*/R from the slope of the line determined by plotting log(β) against 1/T at any certain conversion rate. The modified Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation. Plotting the left hand side for each heating rate versus 1/T at that heating rate gives a family of straight lines of slope -*Ea*/R. The full solution is to be done iteratively by first assuming a value of Ea and then recalculating the left hand side until convergence occurs. Here, a quick solution, however, is also available by moving into the intercept and assuming that it is a constant.

Table 2.3 Kinetic methods used in evaluating activation energy in this study (Liu and Fan, 1998).



Method	Expression	Plots
Friedman (1964)	$\ln(d\alpha / dt) = \ln[Af(\alpha)] - E_a / RT$	$\ln(d\alpha / dt)$ *vs.* $1/T$
Kissinger (1956)	$\ln(\beta / {T_p}^2) = \ln(AR / E_a) + (1/T_p)(-E_a / R)$	$\ln(\beta / {T_p}^2)$ *vs.* $1/T_p$
Flynn-Wall-Ozawa (Flynn and Wall 1966; Ozawa 1965)	$\log \beta = \log \frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567 E_a / RT$	$\log \beta$ *vs.* $1/T$
Modified Coats-Redfern (Brown et al. 2000)	$\ln\left[\frac{\beta}{T^2(1-2RT/E_a)}\right] = \ln\left[-\frac{AR}{E_a \ln(1-\alpha)}\right] - \frac{E_a}{RT}$	$\ln(\beta / T^2)$ *vs.* $1/T$

2.14.2 Modelling of thermally activated reactions

In many cases, DTA/TGA data obtained for composites have been analysed in a purely qualitative manner, i.e. by relating the presence of endothermic or exothermic effects to particular reactions without attempting to obtain quantitative information on these reactions, their progress, or the mechanisms involved. Quantitative analysis is more often performed for isothermal experiments as compared to linear heating experiments. This is related to the availability of isothermal models, which are mathematically simpler than their non-isothermal equivalents (Liu & Fan, 1998).

The type of modeling of thermally activated reactions that has been used in conjunction with DTA, or that can be applied to DTA/TGA, is of a broad and diverse nature. Modelling approaches can mostly be classified as one of four types (Malek et al., 2001):

i. Generic analysis models, which are models that use relatively simple expressions that provide the fraction;

Comment [Kingsley13]: Does this need to change to percent as well?

ii. Transformed as a function of time or reaction rate as a function of fraction transformed, and that are applicable to a wide range of reactions;

iii. Simplified physically based models, which are models that are specifically based on considerations of the physical or chemical process, often with adjustable process-related parameters, such as impingement parameters that allow some flexibility in analyzing data; and

iv. Simulations, which are models that make predictions, often using extensive computer time, with all models of parameters being fixed appeared over the past 10 years and that are suited for analysis of thermally activated reactions in polymer-based composites.

A general objective of the modelling of thermally activated reactions by generic analysis methods and physically based methods is the derivation of a “complete description of the progress of a reaction that is valid for any thermal treatment, be it isothermal, by linear heating or any other non-isothermal treatment. In the case of physically based methods, an additional aim is to be able to use the analysis to understand the processes involved in the reaction. At the outset, it should be realized that for many reactions these objectives are daunting, especially for solid state reactions, any given reaction might progress through a range of mechanisms and intermediate stages, all of which will, in general, have a different temperature dependency (Malek et al., 2001).

2.15 Housing Applications

Fibre-reinforced concrete has proved to be particularly useful in housing projects. A variety of decorative cladding panels have been produced using polypropylene fibre-reinforced concrete in England (Smith & Walker, 1980). Other successful applications include the architectural decoration of both commercial and private buildings with glass fibre-reinforced concrete in England, USA, Saudi Arabia and Japan. Steel fibre reinforced concretes have not been given serious consideration for this application due to the problem of rusting of exposed fibres.

Apart from inorganic and polymer fibres, vegetable fibre reinforced concretes have also proved useful particularly in low-cost housing projects. These fibres when mixed with cement or mortar are used to produce roofing sheets and tiles. In 1979, Swift et al., (1978) reported the production of 2140mm x 69mm x 7mm corrugated roofing sheets with sisal fibre-reinforced cement paste. The sheets were tested in flexure and for permeability and found to be satisfactory. It was reported that sisal cement sheets have an advantage over asbestos and galvanized iron sheets in that they are considerably cheaper and can be manufactured on a cottage industry basis. In 1983, Fageiri (1983) carried out some investigations into the use of Kenaf fibres for reinforcement of rich cement mortar corrugated sheets. Results of the investigation showed that kanaf fibre-reinforced cement mortar corrugated sheet compared favourably with asbestos corrugated sheets. More recently, the Swiss Centre for Appropriate Technology (SKAT) published a comprehensive report on the potential and state of the art of fibre concrete roofing (Odera et al., 2013). In the SKAT report the countries currently producing and using fibres are Bangladesh, Nicaragua and Columbia. The fibres being used are sisal, jute and coir.

2.16 Raffia Palm Fibre

Raffia Palm fibre is a natural plant fibre stripped or peeled out of the raffia palm leaves. It is generally light in weight, flexible, elastic, with small diameter or width and heat sensitive. It has high strength and stiffness which informed the need for this study on its physical and mechanical properties and its impact in composite materials (Odera et al., 2013).

It is cheap and very abundant in regions where it is found, especially in southern Nigeria, Asia, Ivory Coast, Uganda, Cuba etc. Raffia palm fibre is prepared for wearing and used in making clothes, that is, wrappers, tailored clothing and as fashion accessories, such as hats and handbags in Madagascar. Hula skirts in Hawai are 100% raffia palm fibre. Raffia

Palm fibre like other vegetable fibres is an organic component of plant cell wall which cannot be hydrolysed by the digestive enzymes of humans and other monogastric animals. Vegetable fibre consist mostly of the non-digestible Carbohydrate – like or Carbohydrate materials pectin, Hemicelluloses and Cellulose, and the non-digestible non-carbohydrate fraction, Lignin. Another form of fibre, crude fibre, has a long standing and historical usage in texts of animal nutrition.

Two plant materials may contain the same amount of dietary fibre (i.e. pectin + hemicelluloses + cellulose + lignin) and yet have different levels of crude fibre. Crude fibre is a chemical entity. It is the remnant after plant material has been treated with hot concentrated sulphuric acid, alkali, alcohol, or other non-physiological solvents. Hemicelluloses and pectin are the part of total fibre in a vegetable destroyed by acids and alkalis. If a plant material contains negligible quantity of pectin and hemicelluloses, its crude fibre value and behavior will compare favourably with its total fibre content, i.e. it can withstand acids and alkalis treatment. This work reveals the composition of raffia palm and its resistance to alkaline distribution. There are large numbers of raffia palm trees growing in the tropical regions of the world and very abundant in southern Nigeria, where they are tapped for palm wine. The leaves, after the trees are tapped constitute waste which can be utilized for production of new construction materials (Odera et al., 2013).

2.17 Evaluation of Literatures (Summary of Literatures)

In the past, many authors have contributed significantly to mortar and concrete reinforcement. The impact of mortar and concrete reinforcement made in literature by various authors cannot be over-emphasized but can be reviewed in what follows.

Olufemi & Joel (2009) evaluated the suitability of periwinkle shell as partial replacement for river gravel in concrete and observed that periwinkle shells can be used as a lightweight aggregate in concrete works, and also the workability of periwinkle-gravel concrete is reduced with increasing content of periwinkle shells.

Olutoge et al., (2012) investigated the assessment of the suitability of periwinkle shell ash as partial replacement for ordinary Portland cement in concrete and found out that periwinkle shell ash contains all the main chemical constituents of cement though in a lower percentage compared with the Portland cement but also the compressive strength decreased with increase periwinkle shell in the concrete.

Okonkwo et al., (2012) investigated the effects of eggshell ash on strength properties of cement-stabilized lateritic and found out that increase in eggshell ash content increased the optimum moisture content but reduced the maximum dry density of the soil-cement eggshell ash stabilized lateritic soil and also increase in eggshell ash content increased the strength properties of the cement stabilized matrix up to about 35% on the average.

Benjamin et al., (2012) investigated the feasibility of using sea shells ash as admixtures for concrete and made the following conclusion: periwinkle shell ash (PSA), oyster shell ash (OSA) and snail shell ash (SSA) are pozzolanic in nature and satisfy the requirements of ASTM. Therefore, it can be used as a cement replacement material. The initial and final setting times of the blended cement pastes were found to increase with increasing percentage replacement of each of the shell ashes. The compressive strength of the mortar cubes decreases with increase in the amount of the shell ash in the cement paste. The cement can be replaced partially by up to 10% by weight of periwinkle shell ash (PSA), 15% by weight of oyster shell ash (OSA), and 20% by weight of snail shell ash (SSA) in the making of mortar cubes without the strength being affected.

Celik et al., (1996), Sahu et al., (2003), Tripathy & Barai (2006) and Shi-cong et al., (2009) have reported the use of stone dust (SD) as partial replacement of fine aggregate. Celik et al., (1996) reported that increasing the dust content up to 10% improves the compressive strength and flexure strength of concrete. Sahu et al., (2003) concluded that there is significant increase in compressive strength, modulus of rupture and split tensile strength of concrete when sand was partially replaced by stone dust up to 40 percent. Tripathy & Barai (2006) investigated the compressive strength of mortar made with crusher stone dust (CSD) under normal, hot water curing and autoclaving curing. They concluded that up to 40% cement replacement by crusher stone dust and autoclave curing of mortar mix gave same or better compressive strength than the control mortar mix (without CSD and normal curing). Shi-cong et al., (2009) investigated the properties of concrete with crushed fine stone (CFS), furnace bottom ash (FBA) and fine recycled aggregate (FRA) as a fine aggregate. The test results showed that when furnace bottom ash and CSD was used as a fine aggregate to replace natural aggregates, the concrete exhibited higher compressive strength, lower drying shrinkage and higher resistance to the chloride-ion penetration.

Ettu et al., (2013) also reinvestigated the prospects of using periwinkle shell as partial replacement for granite in concrete, and their result showed that this reinvestigation confirms some of the observations made by earlier researchers and particularly strengthens the fact that on the basis of required compressive strength, periwinkle shells could be used as partial replacement of granitic chippings in making concrete for reinforced concrete works.

Ravikumar et al., (2013) work on experimental studies on strength and durability of mortars containing pozzolonic materials observed that there is increase in compressive strength of all the mortar mixes with 12% replacement of cement with pozzolanic material when compared to control mortar, and also that there is increase in flexural strength of all the mortar mixes with 12% replacement of cement with pozzolanic material when compared to control mortar.

Shafana & Venkatasubramani (2014) studied the mechanical properties of concrete with partial replacement of fine aggregate with sugarcane bagasse ash and concluded that the fine aggregate up to 10% can be effectively replaced with sugarcane baggasse ash without considerable loss of workability and strength.

Toledo Filho et al., (2000) also investigated the durability of sisal and coconut fibres when immersed in alkaline solutions. Sisal and coconut fibres conditioned in a sodium hydroxide solution retained respectively 72.7 and 60.9% of their initial strength after 420 days. As for the immersion of the fibres in a calcium hydroxide solution, it was noticed that original strength was completely lost after 300 days. According to those authors the explanation for the higher attack by $Ca(OH)_2$ can be related to a crystallization of lime in the fibre pores.

Ramakrishna & Sundararajan (2005) also reported on degradation of natural fiber when exposed to alkaline medium. Other authors studied date in palm reinforced concrete, reporting low durability performance which is related to fiber degradation when immersed in alkaline solutions (Kriker et al., 2008). Aggerwal et al., (2007), Kim et al., (2011) and Bilir (2012) reported the effect of coal bottom ash as replacement of fine aggregate in concrete. Aggarwal et al., (2007) carried out experimental investigation to study the effect of bottom coal ash. Compressive strength, flexural strength and splitting tensile strength tests were carried out with 0% to 50% replacement. They concluded that compressive strength of concrete containing 50% bottom ash is acceptable for most structural application. Kim et al. (2011) investigated the mechanical properties of high strength concrete. The compressive strength was unchanged and the flexural strength of concrete almost linearly decreased as the replacement ratio of the fine bottom ash was increased. The modulus of rupture was decreased to 19.5% and 24.0% in accordance with 100% replacement of normal aggregates with coarse bottom ash (CBA). It was also found that compressive strength was not affected by the replacement of fine aggregate with CBA. Bilir (2012) investigated the effect of non-ground coal bottom ash (NGCBA) and non-ground granulated blast furnace slag (NGGBFS) on durability properties of concrete. He concluded that replacement of fine aggregate up to 40% NGGBFS and up to 30% NGCBA, concrete has very low chloride permeability.

Khatib (2005), Rakshvir & Barai (2006), Evangelista et al., (2007), Rao et al., (2007) and Soutsos et al., (2011) studied the properties of concrete, incorporating recycled aggregate. Khatib (2005) used recycled fine aggregate to study mechanical properties. The fine aggregate in concrete was replaced with 0, 25, 50 and 100% recycled aggregate. Beyond 28 days of curing, the rate of strength development in concrete containing recycled aggregate was higher than that of the control mix indicating cementing action in the presence of fine recycled aggregate. Rakshvir & Barai (2006) studied recycled aggregate-based concrete. They studied various physical and mechanical properties of recycled concrete. It was observed that compressive strength showed a decrease up to 10% with the increase in recycled aggregate content.

Evangelista et al., (2007) concluded that the use of fine recycled concrete aggregates does not jeopardize the mechanical properties of concrete, for replacement ratios up to 30%. Rao et al., (2007) reported the use of aggregate from construction and demolition waste in concrete. They reported that the use of these waste is suitable for making good quality concrete. Soutsos et al., (2011) concluded that compressive and tensile splitting strength of paving blocks made with recycled demolition aggregate determined levels of replacement which produced similar mechanical properties to paving blocks made with newly quarried aggregates.

Park et al., (2004) reported that compressive, tensile and flexural strength of concrete containing waste glass aggregates demonstrated a decreasing tendency along with an increase in the mixing ratio of the waste glass aggregates. The concrete containing waste glass aggregates of 30% mixing ratio gave the highest strength properties. Shayan et al., (2005) concluded that strength gain was slower in glass powder bearing concrete up to 28 days, but at the age of 404 days all the mixtures exceeded the 40 MPa target and achieved about 55 MPa strength and glass powder also reduced the chloride ion penetrability of the concrete. Idir et al., (2011) investigated the pozzolanic properties of fine and coarse mixed glass cullet. The result showed that the pozzolanic activity increases with glass fineness. Due to this activity, compressive strength of mortar is increased by 10%.

Ghavami (2005) reported the case of a bamboo-reinforced concrete beam with 15 years old and without deterioration signs. Lima et al., (2008) studied the variations of tensile strength and modulus of elasticity of bamboo fiber-reinforced concrete exposed to wetting and drying cycles, reporting insignificant changes, thus confirming its durability.

Zollo et al., (1986), Litvin (1985) and Al-Tayyib et al., (1988) reported that no improvement in the compressive strength of concrete is achieved by the inclusion of polypropylene fibres. However, little improvement is achieved in the tensile and flexural strengths of concrete reinforced with 0.2 percent volume percent of polypropylene fibres. The tensile strength of reinforced sample is 2-8 percent higher than that of unreinforced samples and the improvement in the flexural strength is of the order of 1-4 percent.

Mindess et al., (1988) reported some improvement in the fracture energy and bending strength of concrete reinforced with polypropylene fibres. Their result indicated that as the volume of polypropylene fibres was increased up to 0.5 percent, the maximum bending load increased by about 40 percent while the fracture energy is approximately doubled.

Zonsveld (1975) reported the work conducted at the Building Research Station, England using sisal fibres as reinforcement. The author observed that the use of sisal fibres as reinforcement for concrete required a high over-all water-cement ratio for a workable mix, while the setting time was increased by impurities leaked out of the chopped fibres, and no strength fraction of sisal fibres. However, later investigation by Nilson (1975) and Swift et al., (1978), while appreciating these problems, showed that suitable composite could be made by first mixing the ingredients with about half the measured quantity of water, before adding the remaining water. Where continuous fibres were used, the fibres were precoated with cement paste and placed in alternate layers with the matrix. In both cases, compaction was carried out using a vibrating table. By this procedure, Nilson (1975) reported flexural strength increase of 20-25 percent by the addition of up to 4 percent by volume of sisal fibres. Swift et al., (1978) also showed that sisal fibre additions improved both the flexural strength and ductility of the concrete. They found that the impact strength was only slightly increased by the addition of short fibres, but the use of long fibres phenomenally increased the toughness of the composite. The increase in toughness was of the order of 750 percent, reinforcement in concrete probably because of cost. In their investigation of the influence of jute, coir and nylon fibres on the impact strength of concrete, Sridhara et al., (1971) found that the impact strength of plain concrete was increased by 340 percent by the addition of 3 percent by weight of jute and coir fibres. In the case of the much more expensive nylon fibres, the influence was more phenomenal and an increase of 700 percent was reported.

Uzomaka (1978) investigated the influence of piassava fibre on the properties of concrete and found that the compressive and flexural strength of the fibre-reinforced concrete was not improved relative to the unreinforced concrete. The study was recorded that the workability of the concrete was reduced by the addition of the fibre. In addition to random reinforcement with fibres 100mm in length, Uzomaka considered reinforcement configuration where the ends of the fibre were knotted or tied into a ring. The only property of the concrete improved by the fibre addition is the impact resistance measured on “the ballistic pendulum principle”. The improvement in the impact strength for 5 percent fibre addition is 5 to 16 times that of the unreinforced concrete. The improvement in the impact strength was also found to be a function of the fibre configuration and the orientation of the specimens at test in relation to their casting position.

Raciness & Pama (1978) conducted investigations on potentials of using bagasse fibres as reinforcement for cement with the aim of producing low cost building board. All properties of the composite except water absorption were found to be satisfactory. They proposed reducing the water absorption capacity by painting. It is obvious that given the initial treatment required the subsequent painting required, bagasse-cement roof sheeting would not be as economical as other vegetable fibre-reinforced cement.

In their investigation of the prospect of elephant grass, water reed, plantain and musamba fibres as reinforcement in cement sheets, Lweis & Mirihagalia (1978) found that only elephant grass indicated satisfactory durability in alkaline and rotting environments and thus was the only fibre studied in detail. They reported improvement in the flexural and impact strengths of cement mortar reinforced with elephant grass. The flexural and impact strengths of the reinforced composite were found to be 3.2 and 4.6 times that of the plain mortar respectively. Application of light pressure (about 4.0) for compaction enabled asbestos fibre to be replaced with elephant grass in flat sheets resulting in 80% savings in cost. Obam (1988) reported improvement in flexural and impact strength of 45 and 154 percent respectively. Coir fibre-mortar composite is a low cost roofing material. They found that both the bending and impact strength of the composite were improved by the addition of coir fibre. For 3 percent coir fibre content by volume (which was the optimum for bending strength), the bending and impact strength increases were 25 and 65 percent respectively. In addition to the mechanical properties, they also studied the permeability, water absorption, thermal and acoustic properties of the coir fibre-mortar composite. As would be expected, the addition of coir fibre increased the permeability and water absorption of the composite. For 3 percent fibre content, 4 percent water absorption was reported as against 2.6 percent for the unreinforced mortar. On the other hand, both the thermal and acoustic properties were greatly improved by coir fibre addition. They concluded that coir fibre-mortar composite has good potential as low cost roofing material but more research and performance evaluation are required to improve upon the quality and utilization of the material. Based on the reviewed literature it was observed that extensive work on Raffia palm (fibre and particulate) on polymer modified cement mortar has not been studied to the best of my knowledge, hence this work.

Table 2.4 Properties of Some Common Organic Fibres

Types of Fibre	**Tensile Strenght (N/mm^2)**	**Youngs modulus (10^3 N/mm^2)**	**Ultimate enlogation (%)**	**Specific gravity**
Nylon	759.829	4.14	16.20	1.1
Polypropylene	552.359	0.345	25	0.90
Polyethylene	690	0.14-042	10	0.95
Cotton	414.690	4.83	3-10	1.5
Bagasse	290	17	--	1.24
Coir	72	2.0	10-15	1.33
Elephant grass	180	4.94	3.5	0.30
Water read	70	5.19	1.2	--
Plaintain	92	1.44	60	--
Piassava	143	6	6	0.96
Sisal	570	26	2.6	--
Kenaf	295	22	--	--
Jute	350	32	1.7	--

CHAPTER THREE: MATERIALS AND METHODS

This chapter describes and discusses the materials, equipment and all the general techniques used in this research which include: chemical treatment of the fibers, characterization of the fibers, production of the composites, microstructural analysis, thermal analysis, physical and mechanical properties and statistical design and development of mathematical models.

3.1 Materials

The materials used in this research are: Raffia palm fibre obtained from Awka, Nigeria (see Figure 3.1). They were free of dirt and organic matter, chemical modifiers(NaOH,methanol,etc), polyester resin (Darcon type), 2% solution of cobalt nephthalate and 2% solution of methyl-ethy-ketone (MEK) peroxide were used as accelerator and catalyst, polyvinyl alcohol with molecular weight = 14,000, Appearance: dense, white flakes, Viscosity of 4% aqueous solution ~ 4-6 cps, Ash = max 1% were obtained from Chemical shop in Awka, Dangote 3x cement, 42.5R Grade cement, Portland limestone cement, Nis 444-1:2003-CEM II, B-L42.5R CB-4211 was used for the production of mortar. The most commonly used for structures, roads and all general purpose work where no special properties are required was used; it was stored under dry condition and free of lumps. Very fine sharp sand was obtained from Opi, Nsukka, in Enugu State. The sand was dry and free of salt and impurities. The water used was obtained from tap and it was of high quality and free of oils, acids, alkalies, salts, organic materials or other substances that are deleterious to mortar or any metal in the wall.

Figure 3.1: Raffia palm fibre

3.2 Equipment

The equipment used in this research are: crushing machine, grinding machine, compressive testing machine, analog weighing balance, scanning electron microscope with energy dispersive spectrometer (SEM/EDS), X-ray fluorescence, X-ray diffractometer, beaker, measuring cylinder, Head pan, Trowel, ASeteramTGA-DTA11, and Siemens D-500 diffractometer.

3.3 Methods of Analysis

Comment [Kingsley14]: I added this following the comment by the departmental reviewer. Check if it is fitting.

The methods employed in this project work from preparation of test samples to the final testing of mechanical properties are given chronologically below:

3.3.1 Preliminary work on the raffia palm fibre

Raffia Palm Fibre is a natural plant fibre stripped or peeled out of the raffia plam leaves. It is generally light in weight, flexible, elastic, with small diameter or width and heat sensitive. It hass high strength and stiffness which informed the need for this study on its physical and mechanical properties and its impact in composite materials.

It is cheap and very abundant in regions where it is found, especially in southern Nigeria, Asia, Ivory coast, Uganda, Cuba e.t.c. Raffia Palm Fibre is prepared for wearing and used in making clothes, that is wrappers, tailored clothing and as fashion accessories, such as hats and handbags in Madagascar. Hula skirts in Hawai are 100% raffia palm fibre. Raffia Palm fibre like other vegetable fibres is an organic component of plant cell wall which cannot be hydrolysed by the digestive enzymes of human and other monogastric animals.

Treatment of the raffia palm fibre

a) Raffia palm fibre pre-treatment (mercerization)

The pre-treatment of the raffia palm fibers (RPF) was done by the mercerization process. This pre-treatment partially removes the lignin and other alkali soluble compounds from the fiber surface thereby increasing the adsorption of coupling agents onto the fibres. The fibres with measured average cross-sectional area of 0.8mm^2 were measured into gauge length of 100mm.

Comment [Kingsley15]: Absorption?

Then, six different concentrations (from 0.25M to 2.0M at equal interval) were prepared in covered beakers. The samples of the 100mm fibers were immersed in these NaOH solutions at room temperature. At time interval of 30 mins from 0 to 3 hrs, samples were taken from the different beakers washed with dilute acetic acid, rinsed with distilled water and sun dried differently at 28^{o}c for 6 days. They were placed in light cellophane materials ready for testing.

The physical and mechanical properties of the mercerized fibres were tested for and the best results were obtained for fibres pre-treated with 0.25M NaOH solution for 1hr. Then, other fibre treatment processes were carried out on mercerized fibres pre-treated at these optimal values.

b) Fibre treatment

i) Acetylation (Pre-treated with 0.25M NaOH FOR 1HR)

Comment [Kingsley16]: The reviewer asked you to explain this.

Different concentrations (0.25M, 0.5M, 0.75M, 1.0M, 1.5M and 2.0M) of acetic anhydride in water were formed in beakers. The 0.25M NaOH mercerized fibres were soaked in them. For each concentration, fibres were withdrawn at 30mins interval over a period of 3 hrs, rinsed with distilled water and sun dried at 28^{o}c for 6 days and sent for physio-mechanical testing.

ii) Silane Treatment (Pre-Treated With 0.25M NaOH FOR 1HR)

1% aminosilane solution was introduced into ethanol/water solution of different percentage concentrations ranging from 30/70 to 80/20. The mercerized fibres were soaked in these ethanol/water silane solutions for time ranging from 30 mins to 3 hrs at time interval of 30 mins. At each period, some fibres were removed from the various solutions, sun at 28^{o}c for 6 days, thus dried hydrolyzing the coupling agent.

iii) Potasium Permanganate, $KMNO_4$, Treatment (Pre-Treated With 0.25M NaOH for 1hr)

Comment [Kingsley17]: Write in full.

Six different concentrations of potassium permanganate in acetone were prepared. The mercerized fibres were immersed in each of these solutions for short period of 30 secs, 1 mins, 1.5 mins, 2 mins, 2.5 mins and 3 mins. On withdrawal from the solutions, the fibres were washed with distilled water to stop the reaction of the permanganate on the fibres. They were sun dried 28^{o}c for 6 days and sent for testing.

iv) SLS treatment (Pre-treated with 0.25M NaOH for 1hr)

Comment [Kingsley18]: Write in full.

Ranging from 5% to 30% concentrations, solutions of sodium lauryl sulfate in water were formed. The pre-treated fibres were immersed in the various beakers of the SLS concentrations for time ranging from 30 mins to 3 hrs. After removal of the fibres from the

SLS solutions, they were rinsed properly with distilled water, sun dried, 28^{o}c for 6 days and tested accordingly.

v) Silane Treatment (No NaOH pre-treatment)

This process is same as in the mercerization/silane treatment described above, except that the fibres under silane treatment here are not mercerized. This particular treatment was prompted to verify these results obtained in the combined NaOH/silane treatment

3.3.2 *Carbonization of the Raffia Palm Fibre*

Some of the untreated Raffia palm fibres were packed in the air-tight graphite crucible, fired and placed inside electric control furnace and burned at a temperature of 1200^{o}C for 5 hours to obtain a black colour ash which is the Raffia palm fibre ash (RPFA) which was used in the research (see Figure 3.2).

3.3.3. *Particles Size Analysis*

The particle size distributions of the Raffia palm fibre ash were determined using the American Foundry Society (AFS) specifications. 100g each of the dried ash was taken and introduced in a set of sieves arranged in descending order of fineness and shaken for 15 minutes to achieve complete classification. The weight retained on each sieve was taken and expressed as percentages of the total sample weight. The weight retained on the 100µm was used for the research (see Figure 3.2).

Figure 3.2: Raffia palm fibre ash particles(RPFAp)

3.3.4 The X-ray diffraction (XRD) analysis of the treated raffia palm fibre (RPF)and raffia palm fibre ash particles(RPFAp)

The X-ray diffraction patterns of the RPF and RPFAp samples were determined by X-ray diffraction analysis which was carried out with a Siemens D-500 diffractometer using Co-K_C radiation (K_C=1.79026A). The microscopic study of the ash was determined by JEOLJSM840A scanning electron microscope (SEM) complemented by EDS. All the analysis was carried out at the University of the Witwatersrand, Johannesburg, South Africa.

3.3.5 Density of the treated raffia palm fibre (RPF) and raffia palm fibre ash particles(RPFAp)

The density of the RPF and RPFAp were determined basically by measuring the mass and the volume by using the beam balance and the measuring cylinder respectively. It was then estimated from the formula given as:

$$Density = \frac{Mass}{Volume} \tag{3.1}$$

The density by the water displacement (Archimedean density) allows the determination of the density in air compared to its displacement in water or other liquid of known density (Okafor, 2014, Shi-Chong and Chi-Son, 2009). The determination of the density of the fibre is as follows:

1. Sample of the fibre was weghed accurately using digital HANNA weighing balance and the weight recorded as W_0.
2. The weighed sample material was placed inside a water tight density botlle of known weight nd density.
3. A 500cm^3 measuring cylinder was filed with about 200cm^3 of water and the water level recorded as V_0 considering the concave meniscus.
4. The density bottle containing the fibre was placed inside the measuring cylinder and the new water level recorded as V_1 .
5. Volume of water displaced, $V_1 – V_0$ = Volume of density bottle with fibre, V_c .
6. Volume of the density bottle with fibre, V_C = (volume of fibre V_f) + Volume of desnsity bottle.
7. Volume of fibre $V_f = V_C$ – Volume of density bottle (mass of bottle/density of bottle).
8. Density of fibre = mas of fibre W_0/ volume of fibre $V_{f.}$

3.3.6 Microstructural Analysis

The scanning electron microscope (SEM) JEOLJSM-6480LV and complemented by EDS was used to identify the surface morphology of the RPF and RPFAp. The surfaces of the RPF and RPFAp were examined directly by the Scanning Electron Microscope. The sample was cleaned thoroughly, air-dried and coated with 100Å thick platinum JEOL sputter ion coater and observed SEM at 20kV. The sample was sputter-coated with gold to increase surface conductivity.

3.3.7 Thermal Properties

Thermal decomposition analysis of treated RPF and RPFAp were investigated in terms of global mass loss by using a DTA/TGA Instrument TGA Q50 thermogravimetric analyzer. This apparatus detects the mass loss with a resolution of 0.1micrometer as a function of temperature. The RPF and RPFAp were evenly and loosely distributed in an open sample pan of 6.4 mm diameter and 3.2 mm deep with an initial sample amount of 8-10 mg. Due to different bulk density, the depth of the sample layer filled in the pan was about 1-2 mm. The temperature change was controlled from room temperature (25±3°C) to 900°C at a heating rate 20°C/min.

3.3.8 Fourier Transform Infrared Spectrometry (FTIR) Analysis

Fourier transform infrared spectrometry (FTIR) was carried out on treated RPF and RPFAp as well. IR spectra of the samples were recorded using Perkin Elmer spectrum 100 FT – IR spectrometer in the frequency range 4000 – 400cm^{-1}, operating in ATR (attenuated total reflectance) mode.

3.4 Production of the Composites

Following the recommendations of previous studies, fine sand of particles not larger than 2mm diameter, a mix ratio of cement/sand of 1, water /cement ratio of 0.9, maximum fibers percentage volume of 25, fiber thickness of 4mm were used for the mix according to the previous research of Odera et al (2013); also the polymer volume percent of 5.0 was used (Priya Viswanath and Thachil, 2007). The mixing procedure adopted for all mortar mixes involved the following: (a) measured sand and cement, and mixed them thoroughly until homogeneous mix was achieved; (b) added required quantity of fiber and mixed carefully to a point of uniformity; and (c) added measured quantity of water and mixed the whole lot until a workable mix was obtained.

3.3.4.1 Mixing of Cement and Thermoplastics

Polyvinyl alcohol used was of the hot water soluble grade. It was weighed (5.0 volume percent), added to hot water (80°C) and dissolved by stirring over a period of 15 minutes. The amount of water used for preparing the solution was kept constant to ensure a uniform W/C ratio of 0.9. The solution was used for the preparation of the cement mortar by various RPF and RPFAp from 0, 5, 10, 15, 20 and 25 volume percentage.

3.3.4.2 Mixing of Cement and Thermoset

To prepare polyester resin cement composite the blend of polyester was added to the water-cement mix before the catalyst was added. This in situ preparation of the resin was carried out to avoid the formation of the three-dimensional crosslinked network during the preparation of the composite itself. Initially cement and water were mixed well to form a uniform paste. A mixture of the polyester (5.0 volume percent) with 2% solution of cobalt nephthalate and 2% solution of methyl-ethy-ketone (MEK) peroxide was added to the cement water blend.

3.3.4.3 Casting and Curing

The above ingredients were mixed well to form a homogenous mix which was then cast into moulds. For the production of the RPF composites, the mortar mix was placed in a steel mold, one layer at a time, followed by single layers of long unidirectional aligned fibres. The samples were consolidated using a vibrating table operated at a frequency of 55Hz, resulting in a Raffia palm fiber volume % of 0, 5, 10, 15, 20 and 25. While for the RPFAp composites, the RPFAp was mixed well with the mortar mixture, volume percent of % of 0, 5, 10, 15, 20 and 25 RPFAp each was used and placed in a mould. The samples were also consolidated using a vibrating table operated at a frequency of 55Hz.

Casting was done on a metal mould according to the various tests below. After casting, the specimens were covered in their molds for 24 hours prior to moist curing for 28 days in a cure chamber with 100% RH and 23 ± 1^oC. In the case of the polyester resin composites, the samples were heated in a hot air oven at 120°C for 6 hours to facilitate the crosslinking of the polyester resin. After the samples were annealed to room temperature, they were cured in water for 28 days to complete the curing of the cement. After casting, all the test specimens were stored at room temperature in the casting room. They were demolded after 24 hours, and were put into a water-curing tank for 28 days at room temperature.

3.3.5 Bulk Density Measurements

The bulk density measurements were carried out by determining the weight of the specimen and dividing it by its volume. The same procedure in 3.31.4 above was applied.

3.3.6 Compressive Strength

Compressive strength of hardened cement mortar was one of the basic properties generally evaluated. The compressive strength of the cement composites of thermoplastics and polyester were evaluated after curing the samples for 28 days in water. This evaluation of the cubical specimens of 50mm x 50mm x 50mm dimension (see Figure 3.3) was performed in accordance with BIS 4031 Part 6 1988 (Ettu et al, 2013). The maximum load needed to break the polymer cement composite samples was determined using a Universal Testing Machine, Model No. TUNS 1000(see Figure 3.4).

Figure 3.3: Photograph of samples for density and compression test

The cubes were tested by placing them between the two flat steel platens of the testing machine without any packing. The load was uniformly and steadily applied from zero at the rate of 1 mm/min until failure occurred. The tests were conducted at 1, 3, 7, 14, 21 and 28 days after curing. The compressive strength was evaluated in N/mm^{2}by dividing the maximum load by the cross sectional area of the specimen. The compressive strength was calculated afterwards using the formula below:

$$\text{Compressive strength } (\sigma c) = = \frac{\text{load (P)}}{\text{Area (A)}} \qquad (3.2)$$

Figure 3.4: shows compression test in progress

3.3.7 X-ray powder diffractometry (Xrd)

X-ray powder diffraction technique is the most prominent technique used for unraveling the structure of the materials in bulk and thin film forms. X-ray diffraction is a non-destructive technique used to determine the elements present in any particular substance. X-ray diffraction is based on the fact that, in a mixture, the measured intensity of a diffraction peak is directly proportional to the content of the substance producing it. The samples for X-ray diffraction analysis were prepared in powdered form. The cement mortar sample was taken from the inner core of the matrix. X-ray diffraction analysis (XRD) was done with Philips PW 3071. Diffractometer operated at 45 KV, 40mA with CuKα radiation.

Procedure for Deduction of Minerals

(i) For a given sample, XRD graphs were obtained with intensities on Y-axis and 2θ on X axis.

(ii) d values and intensities of peaks of respective minerals were matched with the fundamental peaks of X-ray powder diffraction files given in the software.

(iii) For any mineral to be present, all the strong peaks were present in the XRD graph to ensure that the mineral was not present.

3.3.8 Scanning electron microscopy (SEM) and energy dispersive spectrum (EDS) analysis

The broken cement mortar samples (with/without polymer modified) collected after compressive strength testing was dried for 24 h at 80°C. The samples were kept in desiccator for over-night to remove moisture. The samples were coated with gold and analyzed by using JEOL-JSM6510 LV scanning electron microscope (SEM) at 20 kV; the instrument was equipped with an energy dispersive x-ray spectroscopy (EDS) facility.

3.3.9 Tensile Test

Direct tensile tests were performed in an Avery Denison Universal testing machine with a capacity of 500KN (see Figure 3.5). The tests were controlled by the cross-head displacement at a rate of 0.1 mm/min. The samples with gauge length of 50mm with fixed-fixed boundary conditions were used (see Figure 3.6). The tensile load, cross head displacement and strain were recorded. The tensile strains were also measured by a strain gage glued on the centre of the specimen, and also the stroke displacement. The stress-strain curves were obtained for the formulations.

Figure 3.5: The Avery Dension Universal tensile test machine

Figure 3.6: Photograph of Samples for Tensile test

3.3.10 Flexural Test

The testing was carried out for 28 days after curing. Flexural strength was determined in accordance with ASTM C 78 - 91 (1991) (Idir and Hamou, 2011). Three specimens (250 mm × 75 mm × 25 mm) were tested for each mixture, and the average strength reported. Three-point bend tests were carried out on the Hounsfield Tensometer 7150 loading frame (see Figure 3.7); the tests were done at a constant displacement rate of 0.25 mm/minute.

Figure 3.7: Photograph of Hounsfield Tensometer

3.3.11 Impact Energy Test

The samples were tested for impact Energy according to ASTM D 1037 (1991). The test was carried out at standard organization of Nigeria (SON) in Enugu. The test was conducted on the Avery Denison impact tester (see Figure 3.8). Each test piece was cut into the standard and evenly supported in rebated square frame without fastenings. Before the test sample was mounted on the machine, the pendulum was released to calibrate the machine. The test samples were then gripped horizontally in a vice and the force required to break the bar was released from the freely swinging pendulum. The value of the angle through which the pendulum has swung before the test sample was broken corresponded with the value of the energy absorbed in breaking the sample and this was read from the calibrated scale on the machine

Figure 3.8: Photograph of Avery Denison impact tester.

3.3.12 Thermal analysis

Thermal decomposition was observed in terms of global mass loss by using a TA Instrument TGA Q50 thermogravimetric analyzer. This apparatus detects the mass loss with a resolution of 0.1 as a function of temperature. The samples were evenly and loosely distributed in an open sample pan of 6.4 mm diameter and 3.2 mm deep with an initial sample amount of 8-10 mg. Due to different bulk density, the depth of the sample layer filled in the pan was about 1-2 mm. The temperature change was controlled from room temperature (25±3°C) to 700°C at a heating rate of 20°C/min. The sampling segment was set as 0.5 second per point.

A high purity Argon was continuously passed into the furnace at a flow rate of 60 mL/min at room temperature and atmospheric pressure. Before starting each run, the Argon was used to purge the furnace for 30 min to establish an inert environment in order to prevent any unwanted oxidative decomposition. The TG and DTA curves that were obtained from TGA runs were carefully smoothed at a smoothing region width of 0.2°C by using least squares smoothing method, and analyzed by using Universal Analysis 2000 software from TA Instruments.

3.3.13 Statistical Design Analysis and Development of Mathematical Model for the Water Absorption and Compressive Strength

Factorial design and linear regression techniques have been widely used in engineering analysis. These techniques consist of plan of experiments with the objective of acquiring data in a controlled way, executing these experiments in order to obtain information about the behaviour of a given process. A full factorial design of experiments of the type P^n (Miller and Freund, 2001) was used in the study. Where n corresponds to the number of factors and P represents the number of levels. Here, i.e., n corresponds to the number of factors (sample condition, V% of RPF and Curing days) and p the number of levels *(P* =2) upper and lower levels of each variable (see Table 3.1).

Table 3.1: Upper and Lower level of each factor along with their coded values

S/No	Variables	Upper level	Lower level
1	Sample condition(A)	Modified(+1)	Umodified(-1)
2	Volume (%)(B)	25 (+1)	0.0 (-1)
3	Curing (days)(C)	28 (+1)	1(-1)

Thus, the number of trial experiments to be conducted for each material is 8(i.e. $2^3=8$). If the response variable wear rate is represented by *Y*, the linear regression equation for these experiments is expressed as(Miller and Freund, 2001):

$$Y=a_o+ a_1A +a_2B +a_3C+ a_4AB +a_5AC +a_6BC+ a_7 ABC \quad (3.6)$$

Where a_o is the response variable at the base level and $a_{1,}$ $a_{2,}$ a_3 are coefficients associated with each variable A (Sample condition), B (volume percent) and C (curing days) respectively; and $a_{4,}$ $a_{5,}$ $a_{6,}$ $a_{7,}$ the interaction coefficients between A, B and C within the selected levels of each variable. The analysis of variance (ANOVA) was also used to investigate which design parameters significantly affected the quality characteristic.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Characteristics of Raffia Palm (Fibres and Particulate)

4.1.1 Density of Raffia Palm (Fibres and Particulate)

The densities of the RPF and RPFAp were found to be 0.21 and 0.3g/cm^3 respectively. These values are lower than the density of Portland cement (1.25g/cm^3) and silica sand (2.4g/cm^3) that were used in the production of mortar; this shows that the addition of raffia palm fibers in cement mortar composites leads to the production of light weight building materials (Odera et al, 2013).

4.2 Chemical Treatment of the Raffia Palm Fibers

4.2.1 Effects of Pretreatments on the Properties of Raffia Palm Fibers

The results of the tensile modulus, tensile strength and % elongation of the pretreatment are shown in Figures 4.1-4.3. From the results, it can be seen that sodium hydroxide (mercerization) pretreatment of the raffia palm fibers has serious effect on the chemical composition and molecular orientation of the cellulose crystallites due to the removal of the hydrophilic commenting substances like lignin and hemicellulose. This process results in a reduced tensile strength of the raffia palm fiber to 89.844N/mm^2 against 128.906N/mm^2 of the untreated fibre. This maximum strength of the pretreated fiber (89.844N/mm^2) is achieved at a NaOH concentration of 0.25M for 1hr. Also recorded here is a positive reduction of water absorption for the untreated fiber (raw) to clean the fiber surface and modify it, in preparation for the chemical treatments.

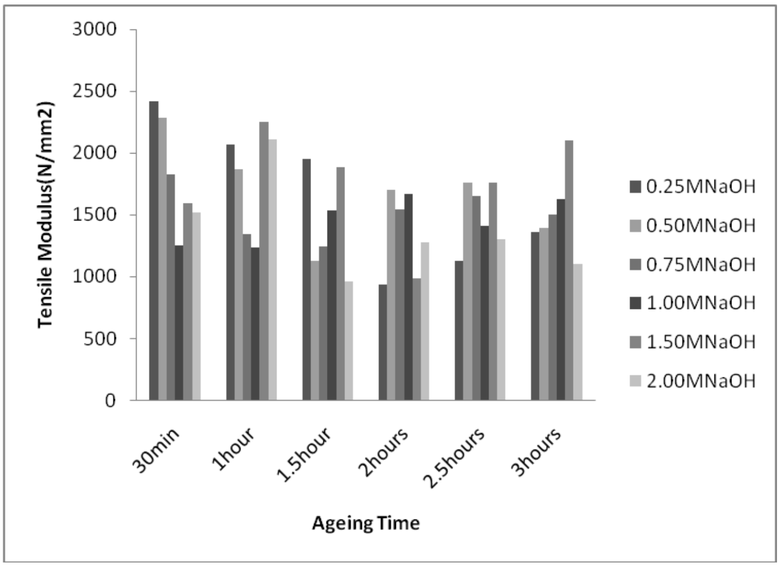


Figure 4.1: Variation of tensile modulus with ageing time

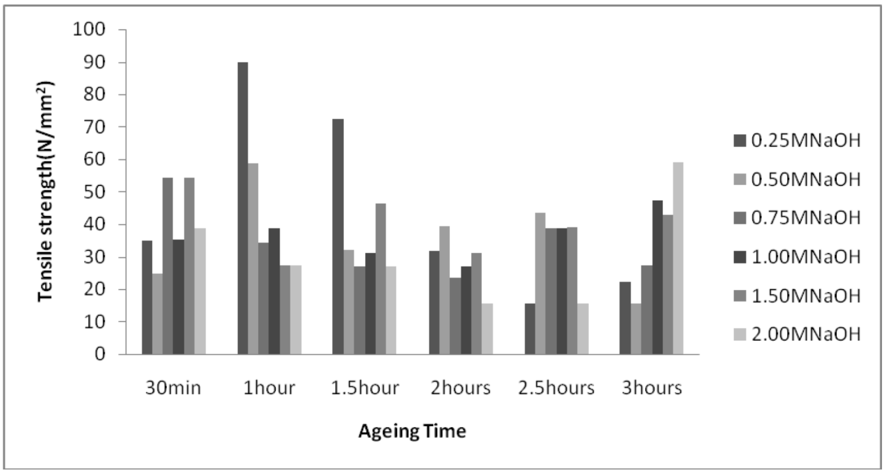


Figure 4.2: Variation of tensile strength with ageing time

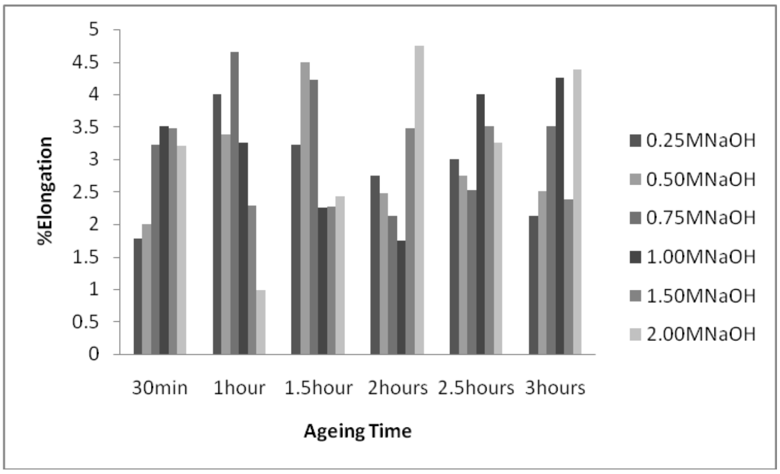


Figure 4.3: Variation of % elongation with ageing time

4.2.2 Acetylation Treatment of Raffia Palm Fibers

The results of the effect of acetylation treatment on the pretreated raffia palm fibres are shown in Figures 4.4-4.6. Also the 0.25M solution of acetic anhydride treatment of the mercerized fibers for 30 mins produced fibre of 25.391N/mm^2 strength, far below the mercerized fibre strength of 89.844N/mm^2 and untreated fiber strength of 128.906N/mm^2, though the water absorption test shows some improvement of 6% water absorption against 12% of the mercerized fibre. This is an overall reduction of about 82% water intake.

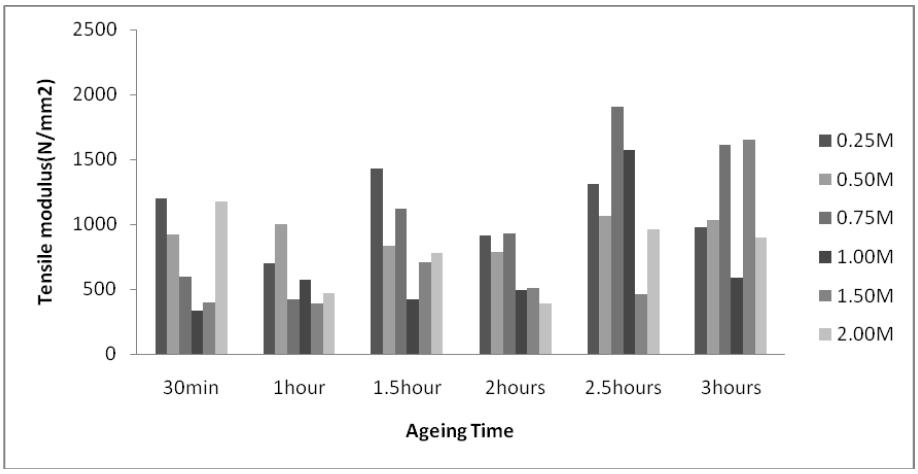


Figure 4.4: Variation of tensile modulus with ageing time for acetylation treatment

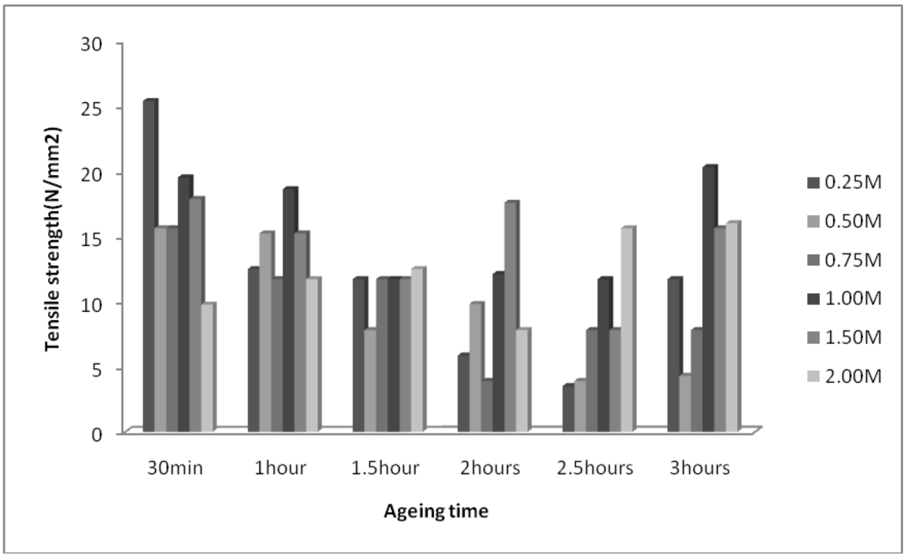


Figure 4.5: Variation of tensile strength with ageing time for acetylation treatment

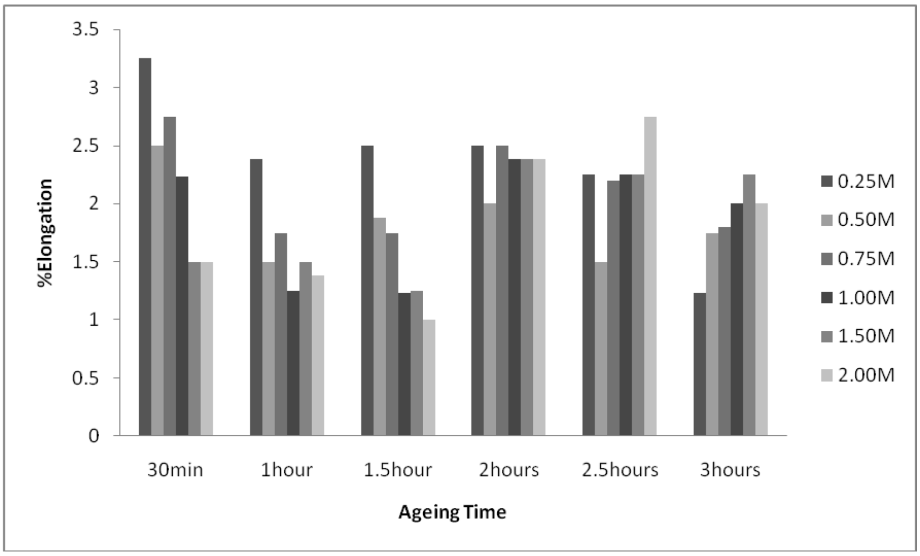


Figure 4.6: Variation of % elongation with ageing time for acetylation treatment

4.2.3 Sodium lauryl sulphate (SLS)

The SLS treatment of the mercerized fibres produces a maximum strength of 72.266N/mm^2 at low concentration of 5% SLS in water for 1hr (see Figures 4.7-4.9). As soaking time increases, the strength decreases. Though with a 70% overall reduction in water absorption, the low strength makes the fibre not good for reinforcement.

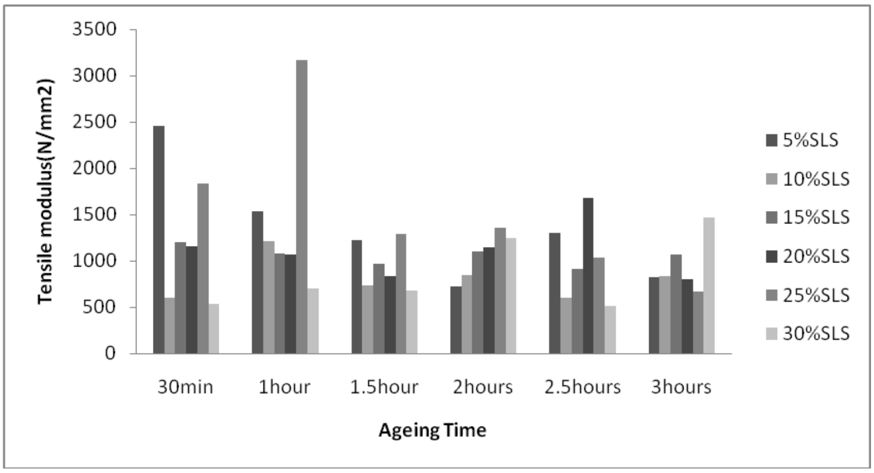


Figure 4.7: Variation of Tensile modulus with ageing time for SLS Treatment

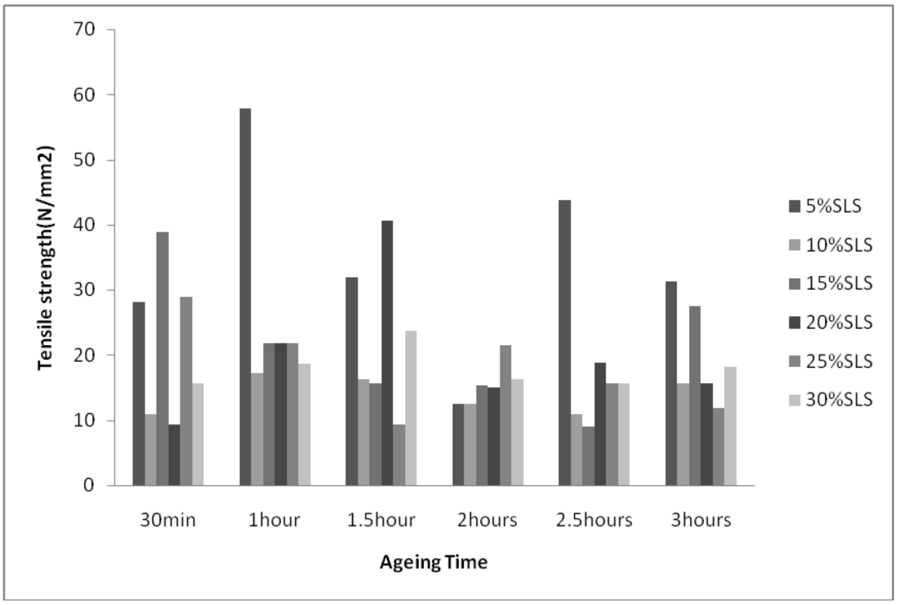


Figure 4.8: Variation of Tensile strength with ageing time for SLS Treatment

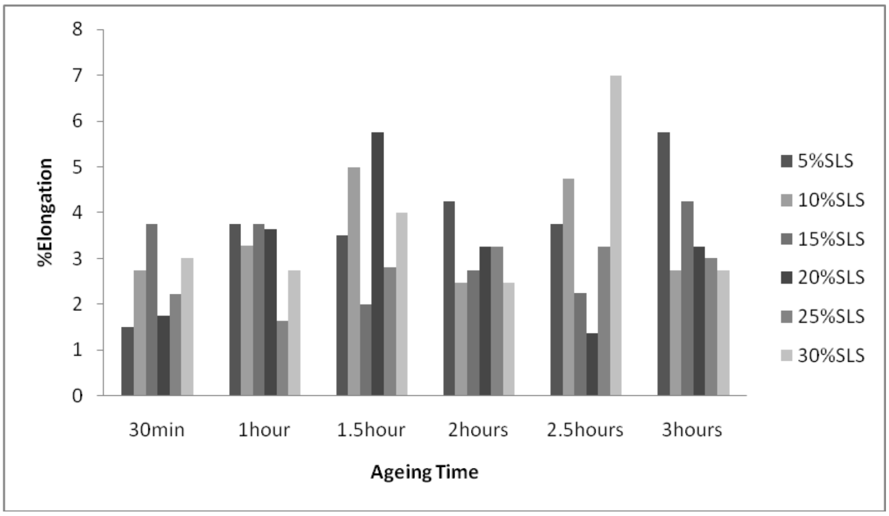


Figure 4.9: Variation of %elongation with ageing time for SLS treatment

4.2.4 Potassium Permanganate (KMno$_4$)

Permanganate treatment of mercerized fibres follows a similar trend with that of sodium laurly sulphate (see Figures 4.10-4.12). Maximum strength is recorded at the lowest treatment time of 30 seconds in 0.5M KMno$_4$ concentration. As the treatment time increases, the effect of the Kmno$_4$ on fiber gets more severe, setting in chemical degradation thereby reducing the strength of the fibre. A water absorption of 8% (which is an overall improvement of 76%) is achieved. The low strength of 42.969N/mm^2 renders the fibers meaningless in composites.

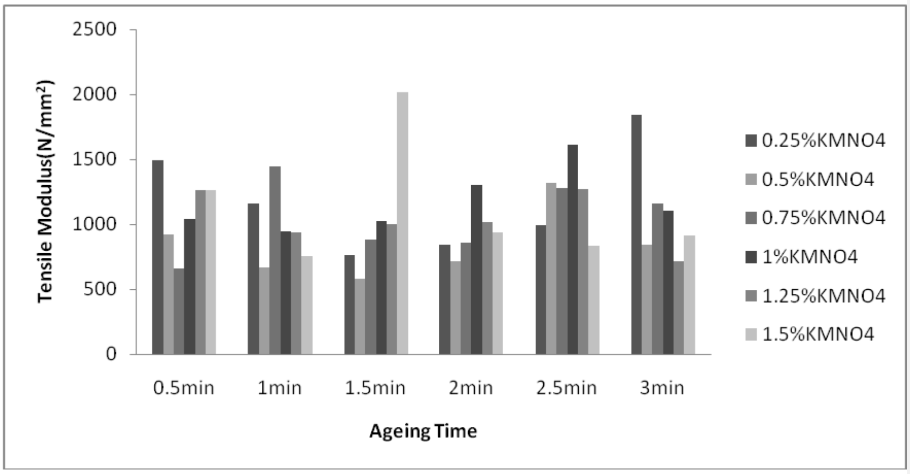


Figure 4.10: Variation of Tensile modulus with ageing time for KMNO$_4$ Treatment

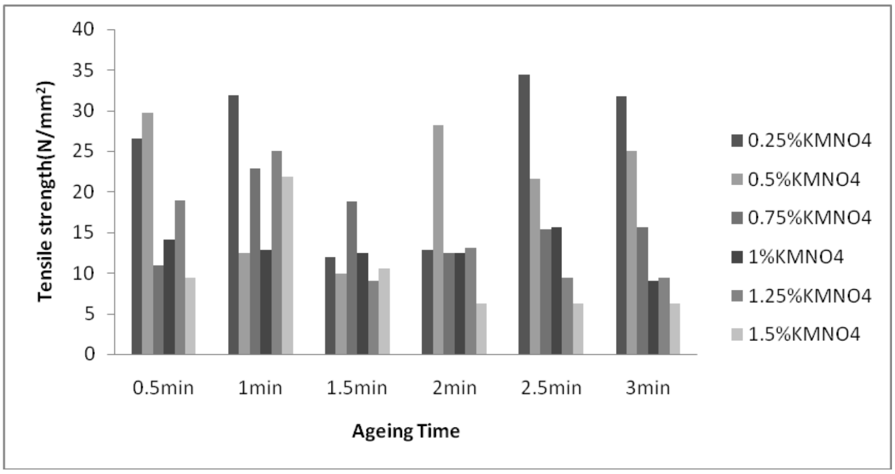


Figure 4.11: Variation of tensile strength with ageing time for $KMNO_4$ treatment

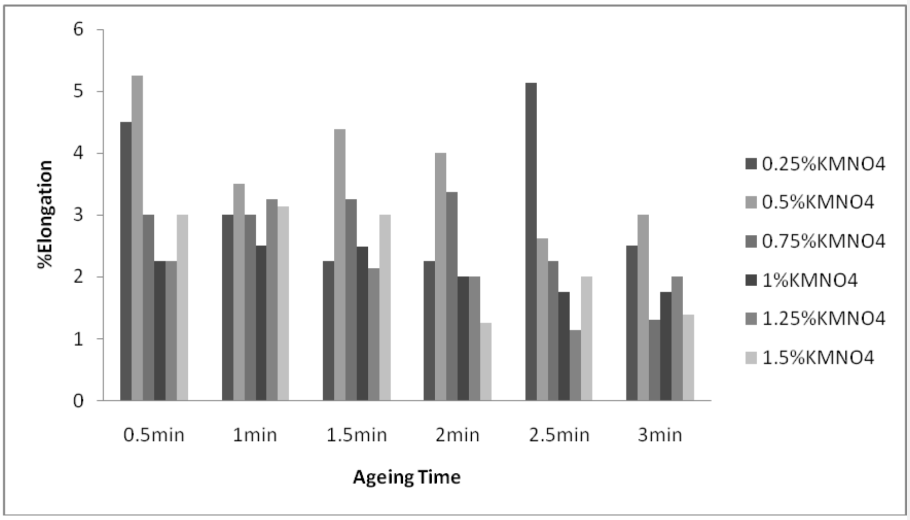


Figure 4.12: Variation of % elongation with ageing time for $KMNO_4$ treatment

4.2.5 Silane

Silane treatment on the mercerized fibers are as shown in Figures 4.13-4.15. From the Figures 4.13-4.15 there are appreciable and significant improvements on the mechanical and physical properties of the fibers. This treatment shoots up the strength of the fiber to 136.329N/mm^2, well above that of the mercerized fiber (89.844N/mm^2) and untreated fiber (128./906 N/mm^2). The key limitation of high water absorbance of plant fiber is hereby drastically reduced to 3% which is an improvement of 91% when compared to that of the raw fiber (34.83%).

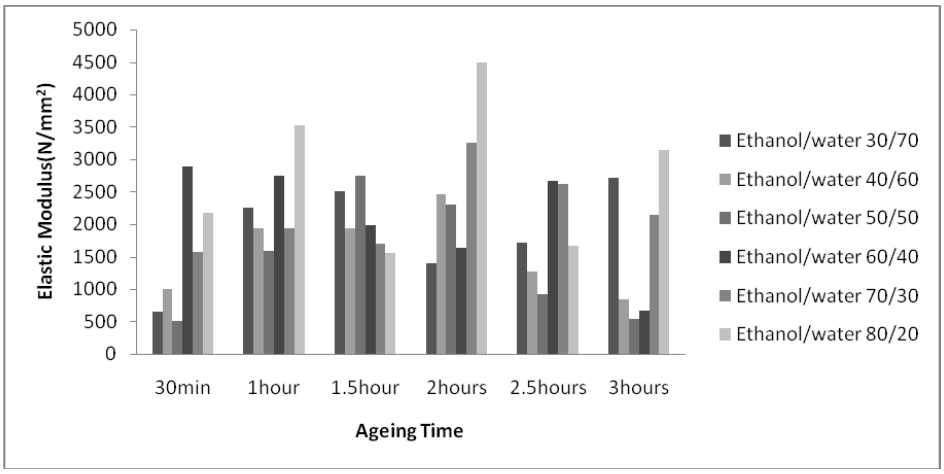


Figure 4.13: Variation of tensile modulus with ageing time for silane treatment

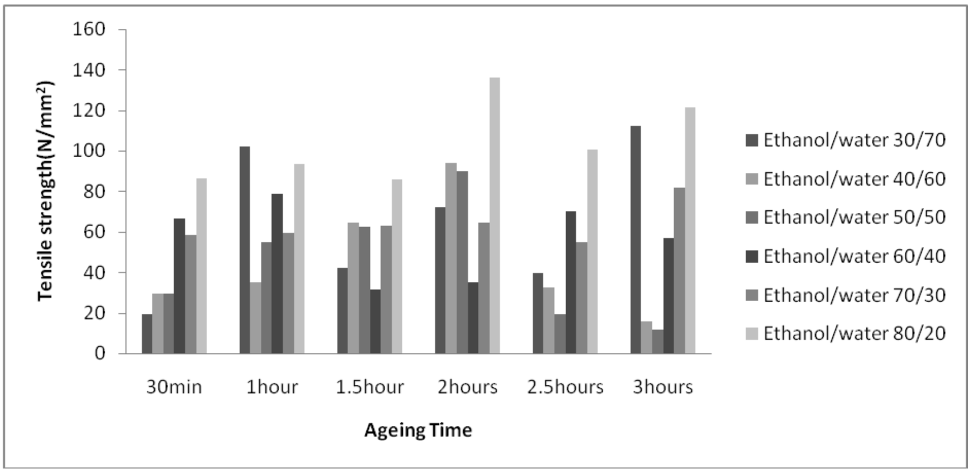


Figure 4.14: Variation of tensile strength with ageing time for silane treatment

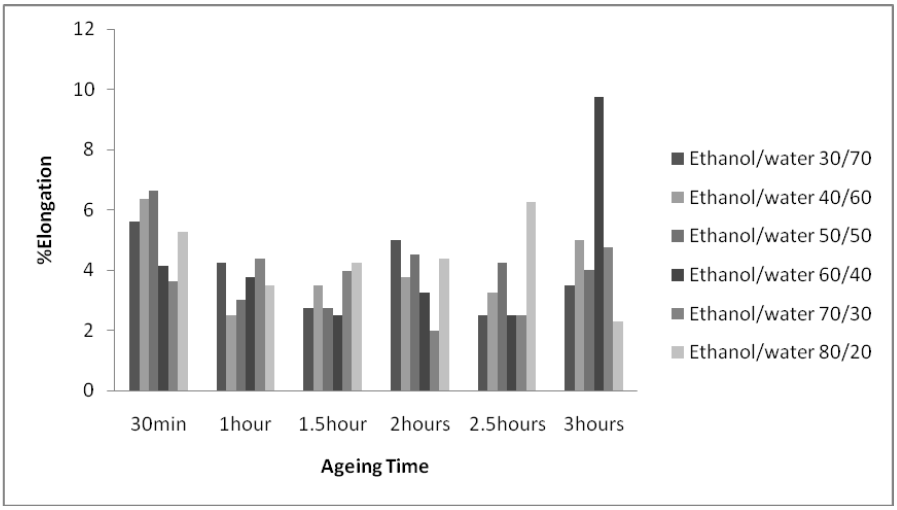


Figure 4.15: Variation of % elongation with ageing time for silane treatment

These improvements could be attributed to the silanols formed by silane hydrolysis and condensation reacting with the fiber hydroxyl groups to form strong and stable covalent bonds. The hydrocarbon chains provided by this process restrain the swelling of the fiber by creating a strong cross-linked network, thus improving on the strength and making the resultant structure less permeable to water. This study shows that a concentration of 80% ethanol in H_2O with silane on the mercerized fibres produces the best results.

This particular investigation reveals that silane treatment is not as harsh as acetylation, sulfate and permangate treatments, rather it initiates intense cross-linking and strong bond formation. The water absorbance of the fibres decreases appreciably in all the chemical treatments. The extension at break of these fibres did not change much. Silane treatments, unlike others, lead to strong covalent bond-formation enhancing the strength marginally. When combined with mercerization, the fibres are significantly rendered fit for composite reinforcement. Because of the best properties obtained for this process, the modeling was carried out to known effect of silanation parameter.

4.2.5 Experimental process design

A full factorial design of experiments of the type P^n was used in the study of the silanation parameter, where *n* corresponds to the number of factors and *P* represents the number of levels. Here, i.e., *n* corresponds to the number of factors (% ethanol/water ratio and ageing time) and *p* the number of levels *(P* =2) (upper and lower levels of each variable, see Table 4.1).

For the modeling of the silanation parameter, the upper and lower level of each variable along with their coded values were used in this investigation as shown in Table 4.1. The design of the experiments and the values of respond variables, corresponding to each set of trial, is reported in Table 4.2. The respond variables, in each trial, represent the average of three measured data at identical experimental conditions. Thus, the number of trial experiments, to be conducted for each material was 4 (i.e. $2^2=4$). If the response variable is represented by *Y*, the linear regression equation for these experiments was expressed as (Miller and Freund, 2001)

$$Y=a_0+ a_1A + a_2B + a_3AB \qquad (4.1)$$

Where a_0 is the response variable at the base level, $a_{1,}$ a_2 are the coefficients associated with each variable A (%ethanol/water) and B *(*ageing time), a_3 the interaction coefficient between A and B within the selected levels of each variable and Y represents tensile strength. The methodology for calculating the values for each regression coefficients, using the coded values A and B of each variable, is described elsewhere. ANOVA was used to determine the design parameters significantly influencing the tensile strength after silanation treatment. The analysis was evaluated at confidence level of 95%, that is for significance level of $\alpha=0.05$ (Miller and Freund, 2001).

Table 4.1: Upper and lower levels of each factor along with their coded values

S/No	Variables	Upper level	Lower level
A	%Ethanol/water	80 (+1)	20 (-1)
B	Ageing time(hrs)	3 (+1)	0.5(-1)

Table 4.2: Matrix design for calculating the regression co-efficient and ANOVA

S/No	X_O	A	B	AB	Tensile strength(N/mm^2)
S1	1	+1	+1	+1	121.3
S2	1	+1	-1	-1	86.32
S3	1	-1	-1	+1	19.53
S4	1	-1	+1	-1	54.67
Effects	70.455	66.710	35.060	-0.080	

Note: +1= upper level, -1 =lower level

From the factorial design and the stepwise variation of the two factors, the estimated response surfaces represents the best fit of the experimentally obtained values. Figure 4.16 showed the estimated response surface for the tensile strength as a function of % ethanol/water and ageing time. It can be seen that both the tensile strength were highly influenced by the % ethanol/water content and ageing time. For as % of ethanol/water increaes from 20 to 80, the tensile strength was found to increase. However, the estimated response surface indicates maximum tensile strength at 80:20% etahanol/water and 3 hours ageing time (see Figure 4.16).

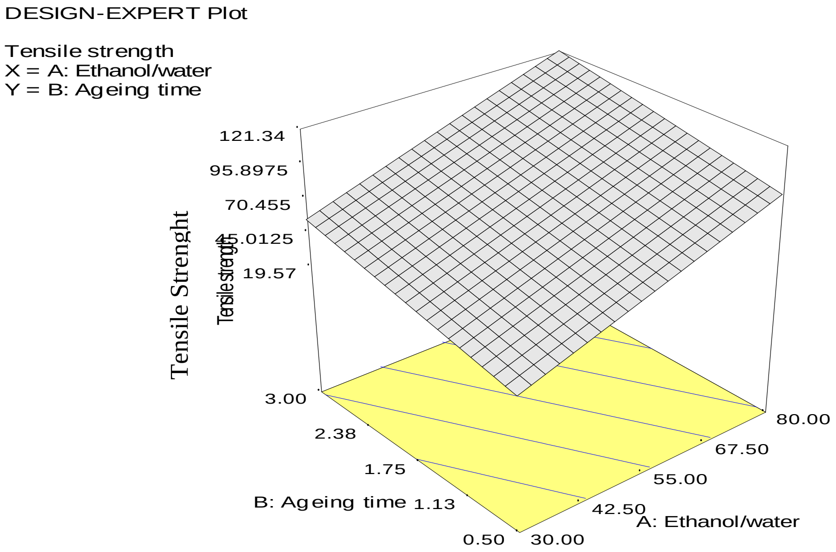


Figure 4.16: Response variation of tensile strength with %ethanol/water and ageing time

ANOVA was used to determine the design parameters significantly influencing the tensile strength. Table 3 showed the results of ANOVA. The analysis was evaluated at confidence level of 95%, that is for significance level of α=0.05 (Miller and Freund, 2001). The last column of Table 4.3 showed the contribution (*P*) of each parameter on the response, indicating the degree of influence on the results. For the ANOVA of tensile strength test, the fit was exact and the R2 value is 1.000. The Model F-value of 443705.29 implies that the model is significant. There is only a 0.11% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A (%ethanol/water), B (ageing time) are significant model terms (Table 4.3). The "Pred R-Squared" of 1.0000 is in reasonable agreement with the "Adj R-Squared" of 1.0000. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 1468.923 indicates an adequate signal. This model can be used to navigate the design space.

Std. Dev.	0.080	R-Squared	1.0000
Mean	70.45	Adj R-Squared	1.0000
C.V.	0.11	Pred R-Squared	1.0000
PRESS	0.10	Adeq Precision	1468.923

Table 4.3: ANOVA for Selected Factorial Model

		Tensile strength				
Source	Sum of Squares	DF	Mean square	F_{value}	P_{value}	Remarks
Model	5679.43	2	2839.7	714.437E+005	0.0011	Significant
A	*4450.22*	1	*4450.22*	*6.953E+005*	0.0008	
B	*1229.20*	1	*1229.20*	*1.921E+005*	*0.0015*	
Residual	6.400E-003	1	6.400E-003			
CorTotal	5679.43	3				

The tensile strength was modeled using Design Expert statistical software. Equation 4.2 was the developed linear regression model for tensile strength (Y).

$$\text{Tensile strength}(Y) = 70.45 + 33.35A + 17.53B \qquad (4.2)$$

Where *(*A) and (B) were the coded values of %ethanol/water and ageing time respectively, the value of a_0 for tensile strength is 70.45. It represents the respond variable value at the base level. By substituting the coded values of the variables for the experimental conditions in Eqs. (4.2), the tensile strength can be calculated. It was noted that from Eqs. (4.2) that the coefficients of A (%ethanol/water) and B (ageing time) were found to be positive. It indicates that increase in %ethanol/water from 20 to 80 raises the tensile strength by (33.35) and ageing time from 0.5 to 3 hrs raises the tensile strength by (17.53).

Confirmation experiments were conducted for four set of conditions. The actual values and the predicted values obtained from the regression model were compared (Figure 4.17). The percentage of error was calculated using Eq. (3) for the validation of the regression model (Miller and Freund, 2001).

% of error = (Actual value - Predicted value)/Actual value×100%   (3)

From Table 18, the average absolute error for the tensile strength is 1.61% , which means that a better accuracy was obtained using the developed regression models. From the chemical treatment the raffia palm fibres treated silane at 80% Ethanol/20%water was used in the work

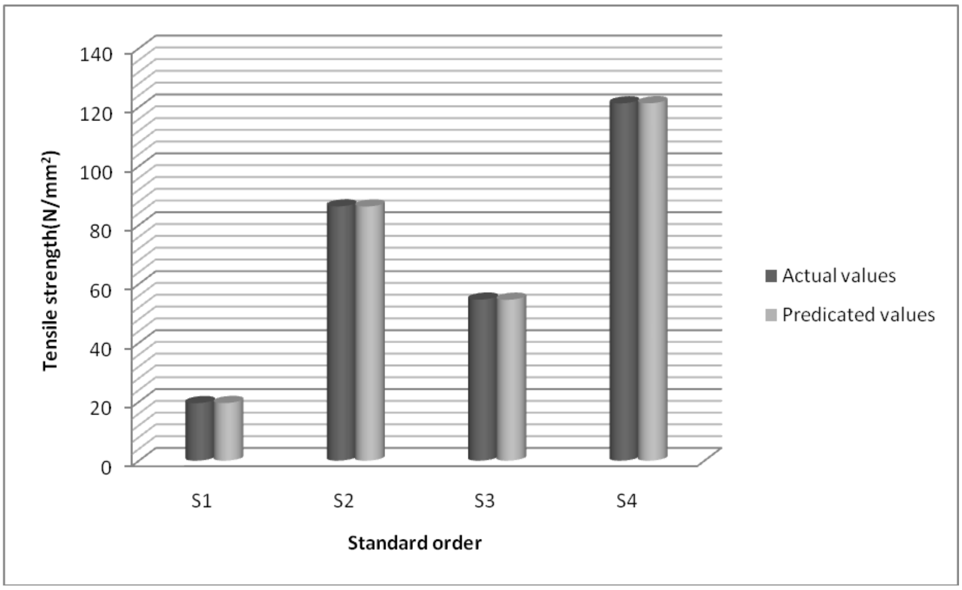


Figure 4.17: Validation of mathematical model

4.3 Morphology of the Fibers

4.3.1 X-ray Diffractometer (XRD) Analysis of Raffia Palm (Fibres and Particulate)

The XRD pattern of the treated RPF and RPFAp are shown in Figures 4.18-4.19. It can be clearly observed that the diffraction peaks appear in the pattern corresponding to phase with good crystalline nature. The higher diffraction peaks of the RPF and RPFAp are 30 and 35.7^{o}C corresponding to SiO_2 and C phases. The XRD pattern of RPFp has similar features to that of RPF but with more diffraction peaks and Carbon phase, which may be attributed to the carbonization of the RPFAp. The grain sizes of the fibres and particles are found to be about

156.7nm and 89.5nm for RPF and RPFAp respectively; Peak broadening depends principally on the crystallite of the crystallite size, the crystallite size and crystallinity index of the RPFAp (25.6%) is higher than the RPF (22.3%).

The removal of the hemicelluloses and lignin in the RPFAp which are amorphous components of the fiber contributes to the increase of the crystallinity index. XRD analysis of RPF and RPFAp showed a diffraction peak at 20^{o}C {001}, which is designated to graphitic carbon. Moreover, peak at 43^{o}C is also seen in the Figure 2 that is known to be associated with carbon {111}. A small peak present at 78^o of XRD of Raffia palm fiber depicts the presence of the Silica. However, the graphitic peaks are not very prominent in RPF samples. With the presence of hard phases of SiO_2, C, in Raffia palm fiber means, it has similar composition with other biomass currently used in building construction (Aggarwal, 2007; Bing and Juanyu, 2007).

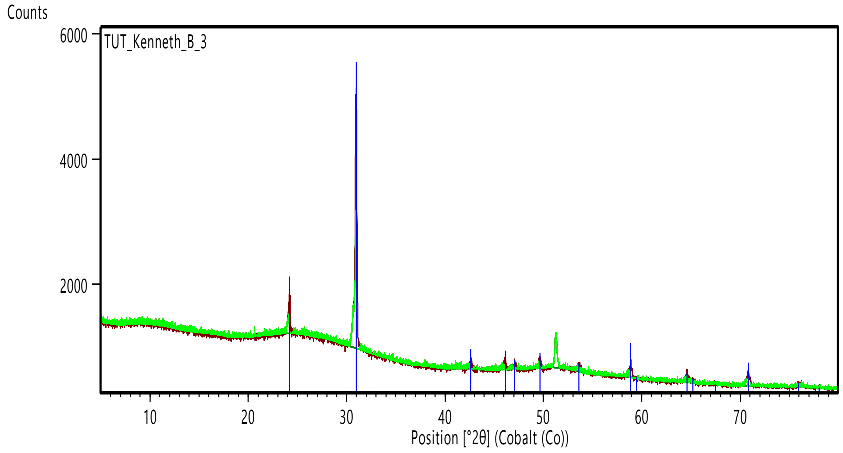


Figure 4.18: XRD spectrum of treated RPR

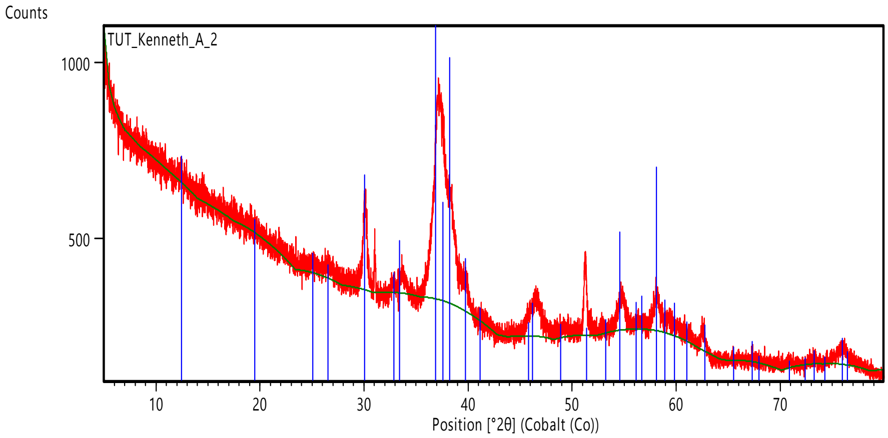


Figure 4.19: XRD spectrum of RPRAp

4.3.2 Scanning Electronic Microscope Analysis of Raffia Palm(Fibres And Particulate)

The morphology of the raffia palm fibres was investigated using SEM. Figures 4.20-4.22 shows the SEM image of the RPF and RPFAp

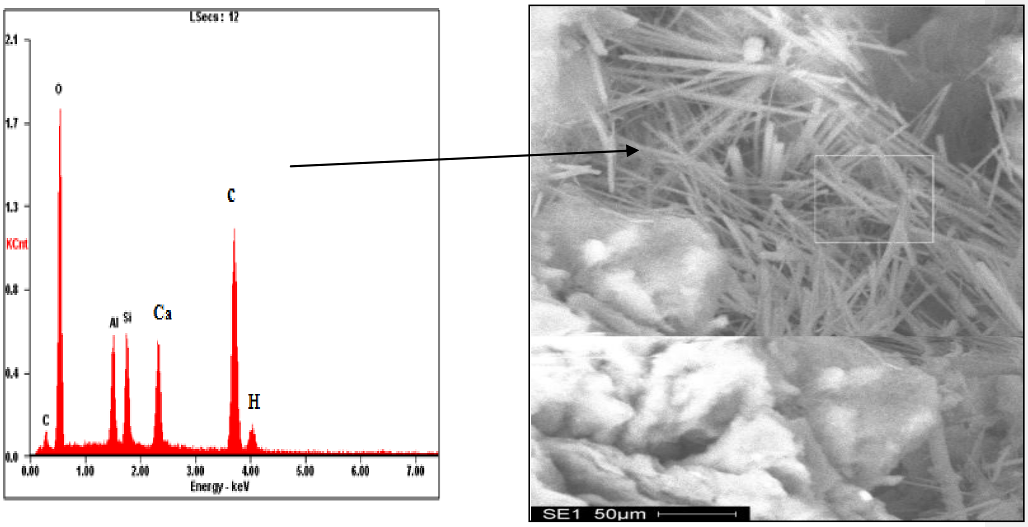


Figure 4.20: SEM/EDS of Raffia palm fibers

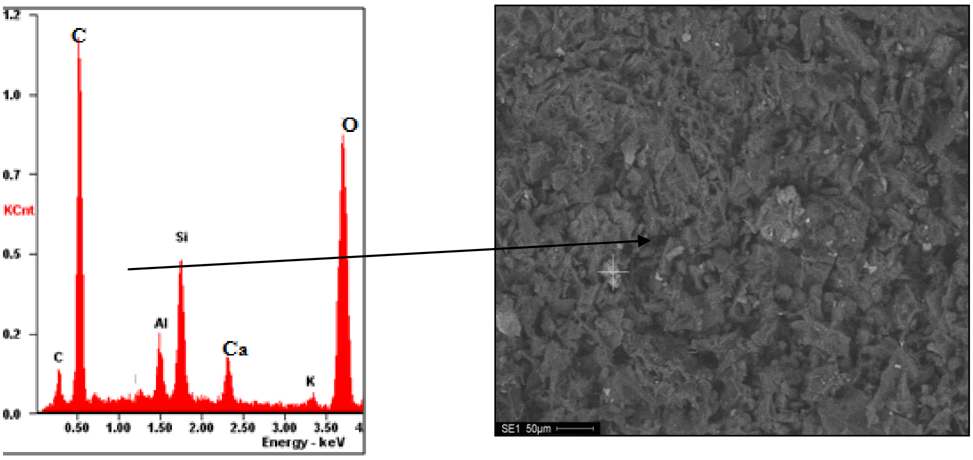


Figure 4.21: SEM/EDS of raffia palm fibers ash particle

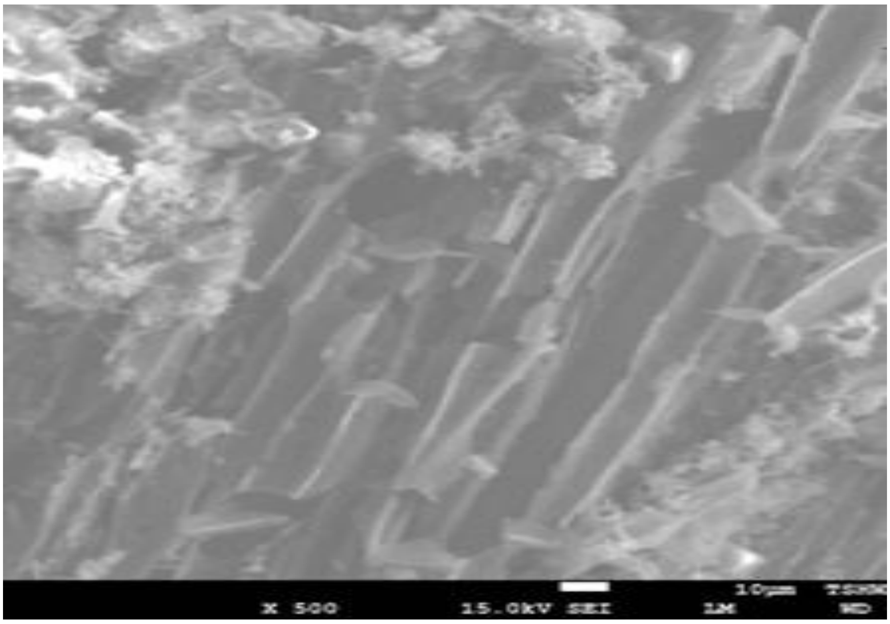


Figure 4.22: SEM of treated raffia palm fibers

The spherical shaped particles distributions are visible through the SEM analysis of the RPFAp (Figure 4. 21). From the SEM analysis of the RPF it can be observed that the fibres are not roundish but longitudinal in shapes and continued form which confirms that the fibres can be used for continuous fibre fabrication. The fiber/particles surface morphology plays a vital role in case of composite materials. But the treated fibres are more clean, straight and longitudinal.

External features of particles such as contours, defects, damage and surface layer were not seen in the SEM. Energy dispersive spectrometer (EDS) used for the microanalysis to quantify the elements in the raffia palm fibres show that the RPFAp has higher carbon(C) peak than the RPF. This is attributed to the carbonization of the raffia palm fibers. The RPF has elements such as C, H, O which are major peaks that confirm the organic nature of the RPF (see Figure 4.20).

4.3.3 Atomic Force Microscope (AFM) Analysis of Raffia Palm (Treated Fibres and Particulate)

The surface topography was studied with atomic force microscope (AFM) measurements to determine the grain size dimensions of the RPF and RPFAp . Figures 4.23-4.24, show the 2D and 3-D AFM images of the RPF and RPFAp. In RPF images, uniform crystallites with small grains were found affirming the morphological result obtained from scanning electron micrograph. In RPFAp. the growth of spherical crystallites cover the entire surface, thereby giving it a uniform appearance and finer grained texture (Figure 4.24). Figure 4.23 also reveals the longitudinal nature of the Raffia palm fibres which is more visible in the 2D-AFM pattern.

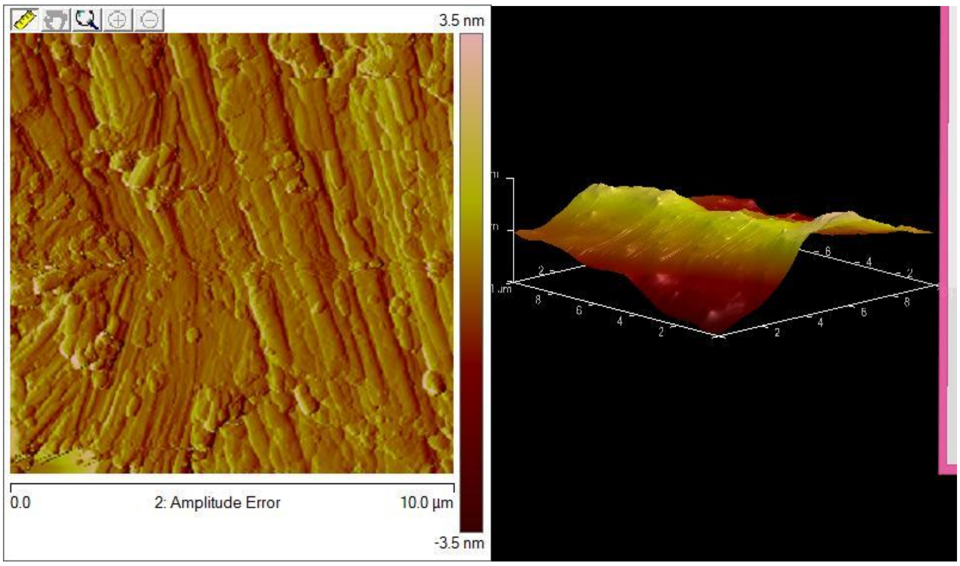


Figure 4.23: the 2D and 3D AFM pattern of treated Raffia palm fibers

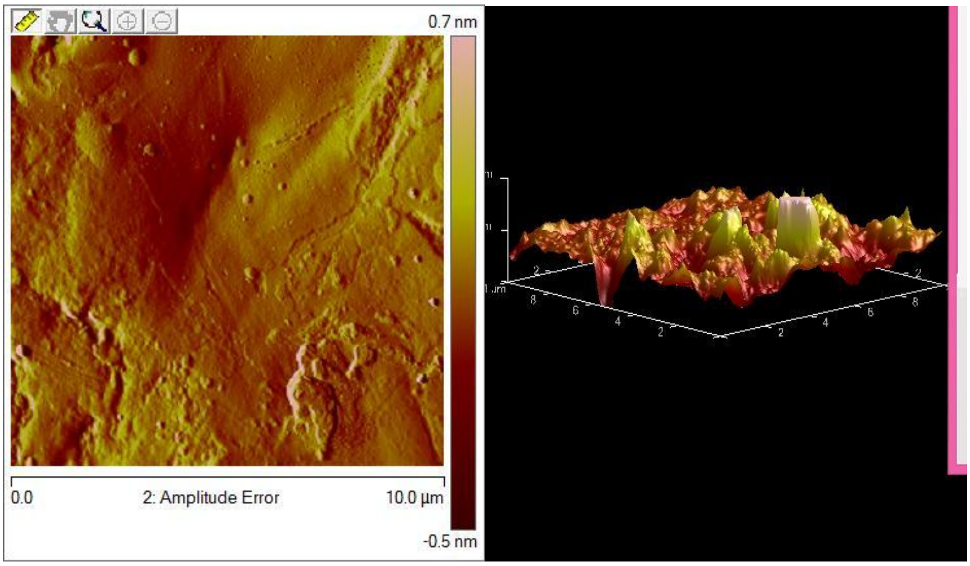


Figure 4.24: The 2D and 3D AFM pattern of raffia palm fiber ash particles

4.3.4 FT-IR Spectroscopy of Raffia Palm (Treated Fibres and Particulate)

FT-IR spectroscopy is an effective tool for studying the physico-chemical and conformational properties. Figures 4.25-4.26 and Appendix Tables A5-A6 show the FTIR spectra of RPF and RPFAp. Their broad peaks range from 324.04-3047.53cm$^{–1}$ and 324.04-3950.22 cm$^{–1}$ for RPF and RPFAp respectively. The peak broad at 3047.53 cm$^{–1}$ is assigned to the hydroxyl groups (–OH) of RPF. The peak at 2600.04-2908.65cm$^{–1}$ related to C–H stretching and 1782.23 cm$^{–1}$ is attributed to C¼O stretching of carboxyl groups from hemicellulose. The small peak presence at 1581.63 cm$^{–1}$ is indicated as conjugated C–O group from aromatic skeletal in lignin. The peak at 1442.75 cm$^{–1}$ is corresponding to CH_2 deformation vibration of cellulose. Moreover, the peak at 13656 cm$^{–1}$ is referring to C–H group deformation in cellulose and hemicellulose. A peak found at 1280.73 cm$^{–1}$ is assigned as C–O groups from acetyl group in lignin. Another broad peak detected at 1049.28-1195.87 cm$^{–1}$ is C–H group vibration in cellulose. The peaks in the 324.04–87.54cm$^{–1}$ range related to C–H vibration of lignin. The stretching of carbonyl group which disappeared in RPFAp may be due to the removal of side chain of acetyl group of acetylated xylan by carbonization at elevated temperature.

Comment [Kingsley19]: Check

The absence of absorption band between 1350cm^{-1} to 1600cm^{-1} in the RPFAp may further confirm the complete removal of lignin during carbonization process. The FTIR spectrum of the RPF and RPFAp shows a change of peaks from 1689.64 cm^{-1} to 1651.97 cm^{-1}, which indicates the reduction of carboxyl groups in the RPFAp structures. The change of peaks from 1782.23 cm^{-1} to 1743.65 cm^{-1} confirms that in the RPFAp, the absorption band of C=O group is more due to carbonization. This can also be observed in the reduction of OH groups from 3047.53 cm^{-1} to 2954.95 cm^{-1}

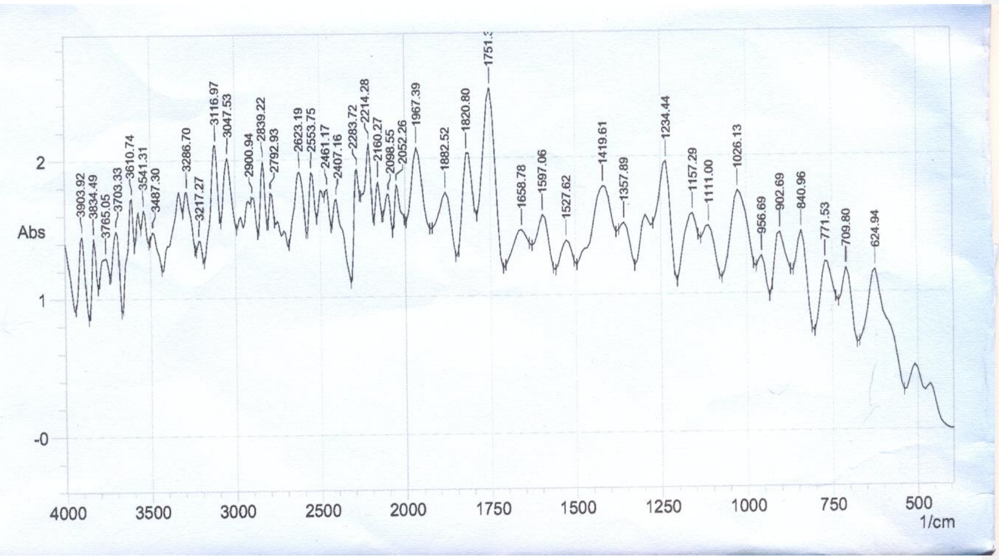


Figure 4.25: FT-IR spectroscopy of RPF

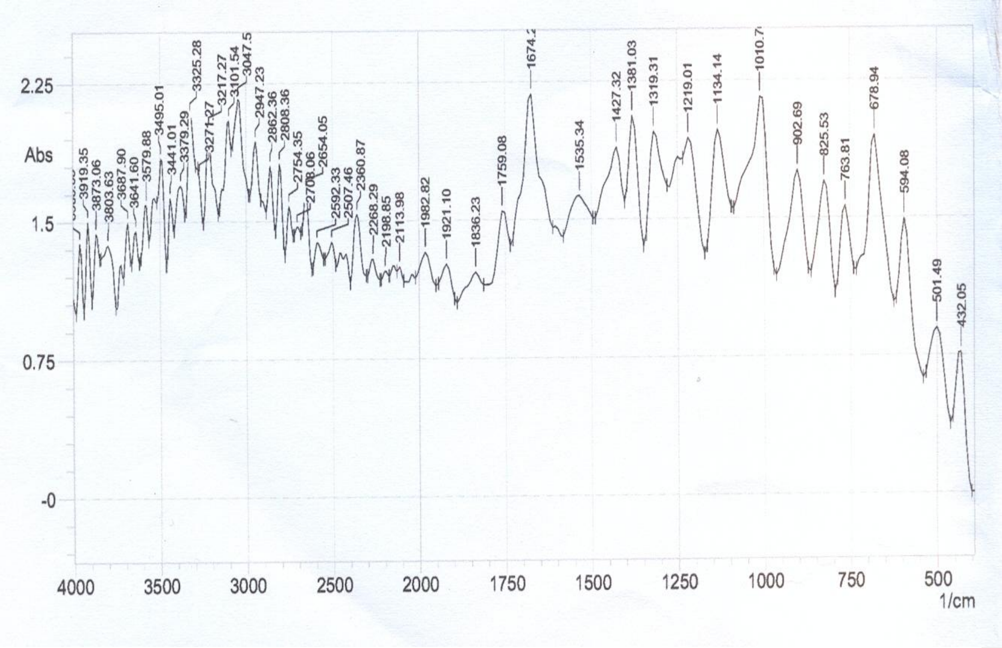


Figure 4.26: FT-IR spectroscopy of RPFAp

4.3.5 Thermal Analysis of Raffia Palm (Treated Fibres and Particulate)

The TGA/DTA curves of the RPF and RPFAp are shown in Figures 4.27-4.28. The temperature at the maximum rate of weight loss (T_{dmax}) is 234.5 and 600.56^{o}C for RPF and RPFAp respectively. The T_{dmax} of the Raffia palm fibres increased after carbonization. This indicates that the improvement of the thermal stability occurred due to char formation. The char became like a protective barrier that prevented the thermal decomposition of the Raffia palm fibres. This will form a better char formation, thus leading to a higher thermal resistance.

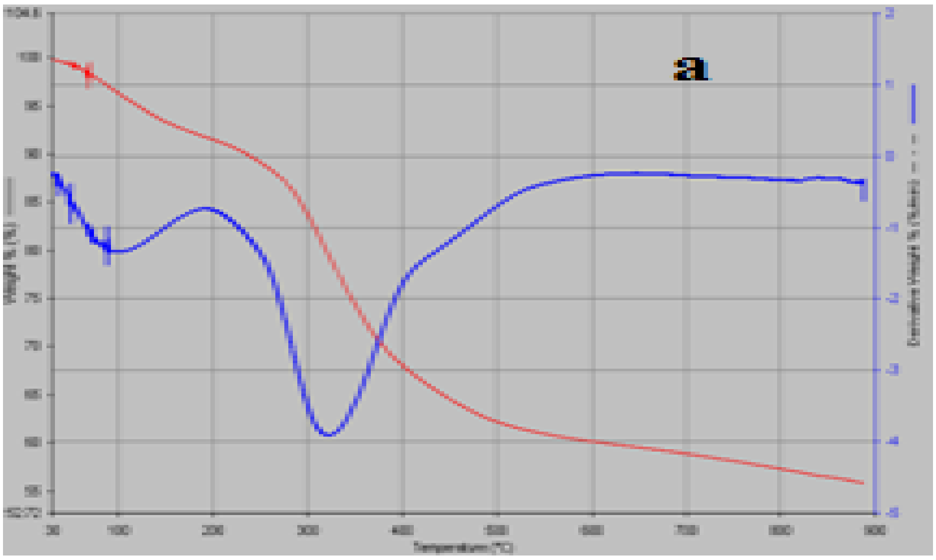


Figure 4.27: TGA/DTA of RPF

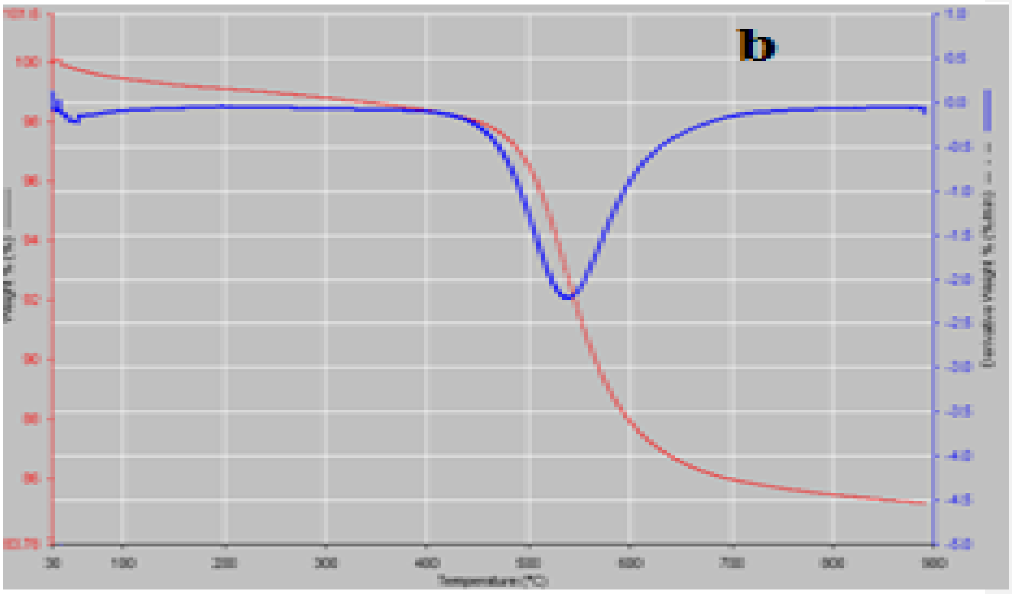


Figure 4.28: TGA/DTA of RPFAp

It can be seen from the DTA curve that the total burning/degradation of the residual particle took place in the above temperature interval. The vaporization of water took place at the first endothermic peak, the burning of cellulose and volatile matter took place between the first endothermic peak and the last endothermic peak; while at the last peak, the maximum thermal decomposition occurred. Thus, the endothermic effects on the raffia palm fibres are seen in three progressions: dehydrogenation, evaporation of some cellulosic materials and the thermal decomposition of the material. The overall effect is seen in the decreased mass of the sample.

On the other hand, the heat flows which are shown as DSC curves of Figures 4.29-4.30 predict that the huge rates of mass losses in the TGA/DTA curve for RPF could not contribute to the exothermic performance of this sample at expected level. This is because the most of the mass losses are formed from the elimination of the volatiles such as carbon dioxide which play no important role on the calorific output. The exothermic regions for all the samples either comprised of two different parts or a unique broad peak having a shoulder, representing the effects of both homogeneous combustion of volatiles and char burning. Also the maximum peaks occurred around 200^{o}C (heat flow 1.4w/g) and 550^{o}C (heat flow 25w/g) for RPF and RPFAp respectively. The DSC scan can also support that carbonization also improved the thermal stability of the Raffia palm fibres.

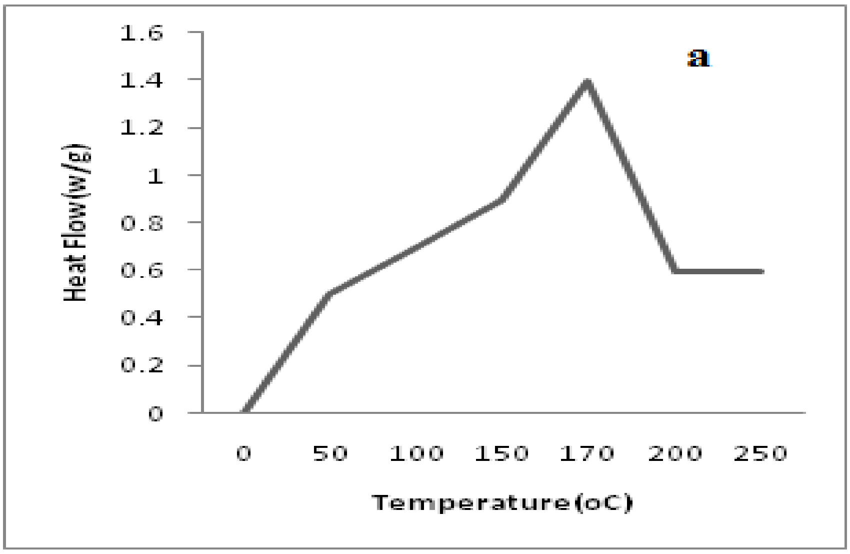


Figure 4.29: DSC scan of RPF

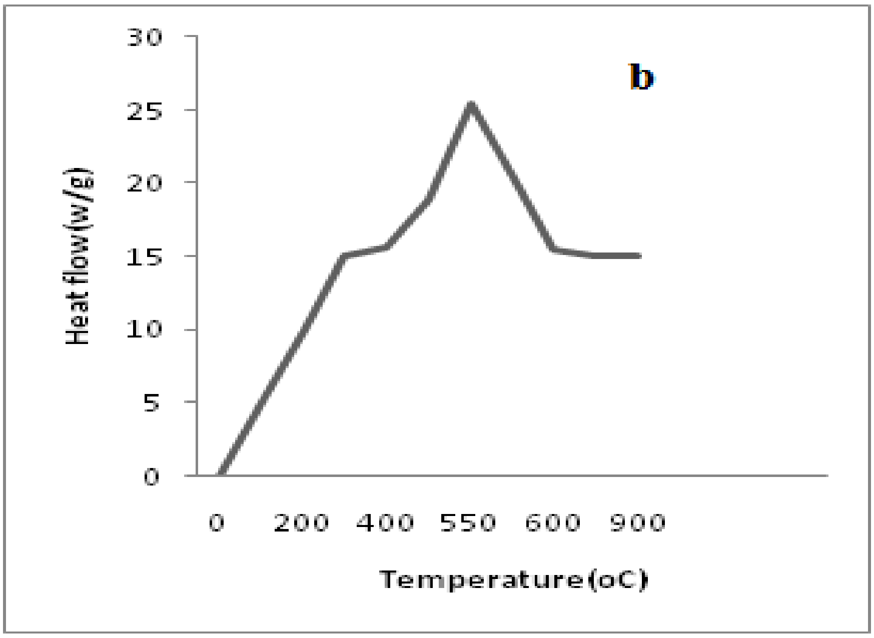


Figure 4.30: DSC scan of RPFAp

4.4 Phyical Properties of the Composites

4.4.1 Visual Observation

There was no crack on the samples after production and curing, for the polymer modification influences the properties of a fresh concrete mixture as well as the properties of its hardened version. Some effects of polymer addition are: improved workability and retardation of the cement hydration. The effects are due to the presence of surfactants in the polymer emulsion. These surfactants also enhance workability of the fresh cement mortar mix. The encapsulation of cement particles by the polymer molecules and the retention of water by the surfactants cause partial or complete retardation of the hydration of the cement.

The modification of the hardened cement mortar is mainly due to the formation of the polymer film, which results in improved adhesion between the cement particles. The polymer modification also contributes to reduced porosity, bridging of micro fractures and improved bonding between the cement and the aggregates. The presence of the polymer particles prevents the formation of large crystals that are formed during the cement hydration. The distribution and development of the polymer in the cement matrix also contribute greatly to the improvement of mechanical properties of the cement concrete.

4.4.2 Density of the Composites

The result of density measurements on the unmodified and polymer modified cement mortar materials are shown in Figures 4.31-4.32 and Table A7 (Appendix A). From the Figure 4.31-4.32, it was observed that the density of the cement mortar composites with decreased Raffia palm (RPF and RPFAp) additions increases in the formulation of the mortar, due to low density of Raffia palm (RPF and RPFAp) which are lower than the density of cement. Also from the results, it was observed that the density of RPF cement mortar composites was lower than the density of the RPFAp composites. The PVA modified cement mortar offered higher density of all of them, because water-soluble polymer such as PVA, the molecular weight, has an influence on its reaction with the Ca ions in the cement. The polymer with lower molecular weight forms coordinate bond with the Ca ions thereby forming a denser network of the polymer cement matrix leading to greater density. This shows that composites with light weight can be made with this RPF. The result is in line with the earlier work of Benjamin et al (2012), Priya and Paul (2002).

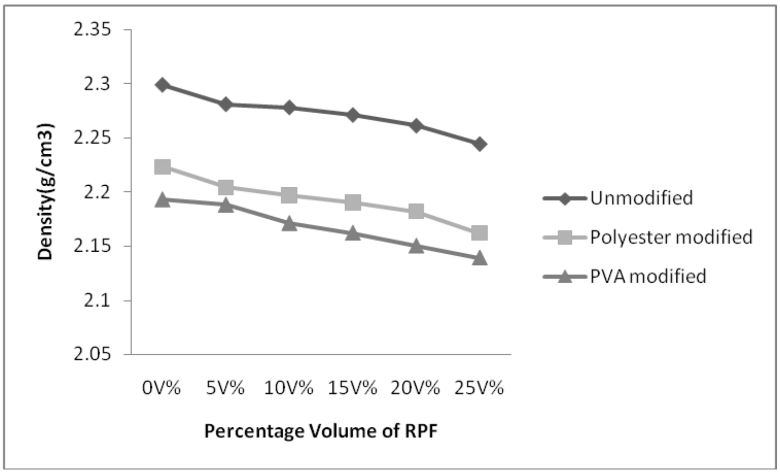


Figure 4.31: Variation of Density with Volume percentage of RPF

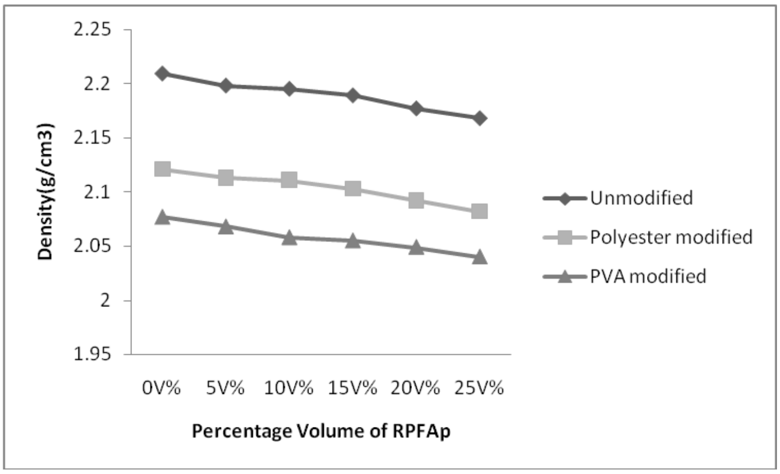


Figure 4.3.2: Variation of density with volume percentage of RPFAp

4.4.3 Water Absorption

The results of the percentage of water absorption for the various formulations are shown in Figures 4.33-4.38 and Appendix A (Tables A8-A9). The results showed that as the curing days increased there was great reduction in the percentage of the water absorption for all the formulations; this can be attributed to the strong bonding achieved in these samples during curing. During the curing of cement paste, the matrix becomes denser due to the formation of various hydration products. Hydration is a continuous process. The rate of hydration is high in the initial period but decreases with time. On the contrary, in the case of polymer-modified cement, hydration proceeds gradually due to the formation of the polymer film around the cement particles which also helps the reduction rate of water absorption. Hence the slightly lower values of water absorption for these cases gives the changes undergone during cure of different composites.

Also the RPF formulation samples have higher % of water absorption than the RPFAp samples; this was because in the RPF samples the fibres will not totally mix up with the cement mortar to become one body as that of the RPFAp composites where there is almost homogeneous mix-up of the RPFAp and the cement mortar which, leads to the reduction of the water absorption. Also during casting, water tends to settle around the fibres due to their hygroscopic nature, creating zones of increased water-to-cement ratio and thus, increased water absorption. It is seen that polymer-modified cement pastes have undergone minimum water absorption. This may be due to the sealing of the pores and voids by the polymer which possibly prevents the entry of water into the polymer cement matrix, thereby inhibiting water interactions. These results indicate resistivity of the composite against deterioration when exposed to water.

The PVA-modified cement mortar has a higher percentage of water absorption than the polyester-modified samples because in the water-soluble polymer, cement composites seem to have bonded to the water by the hydrogen bonds resulting in water retention in the matrix than the polyester modified cement mortar. The low values of water absorption recorded in this work for the polymer-modified cement mortar after curing for 28 days are within the recommended standard of 0 to 2% for roofing sheet application (Shi-Cong and Chi-Sun, 2009; Saxena et al, 2008).

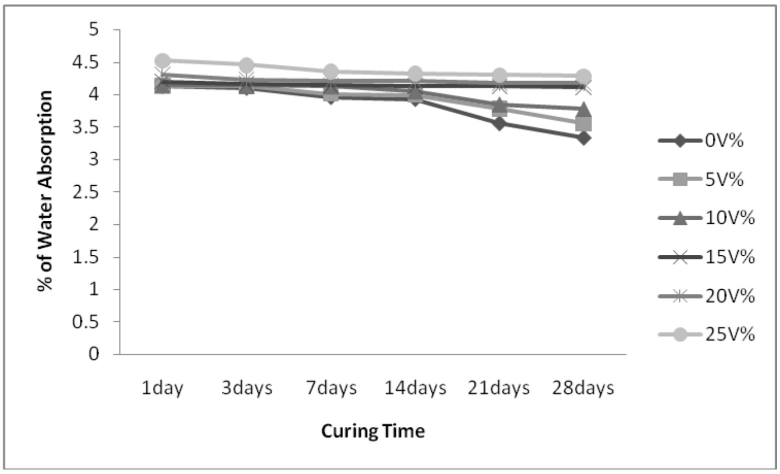


Figure 4.33: Variation of % of water absorption with number of days of curing for unmodified cement mortar/RPF

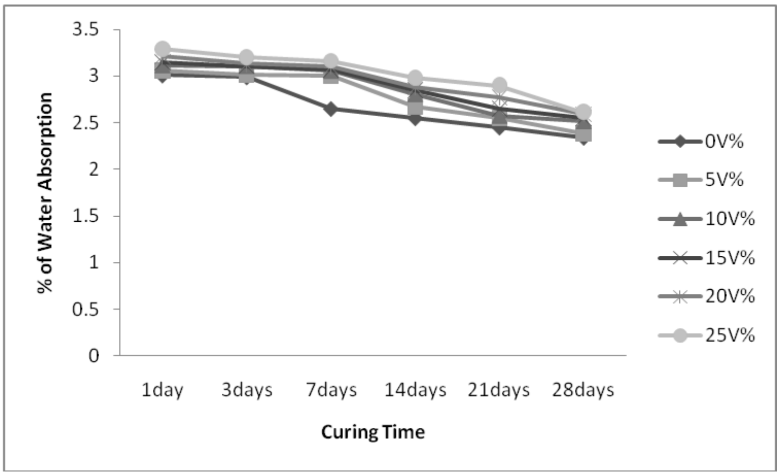


Figure 4.34: Variation of % of water absorption with number of days of curing for PVA modified cement mortar/RPF

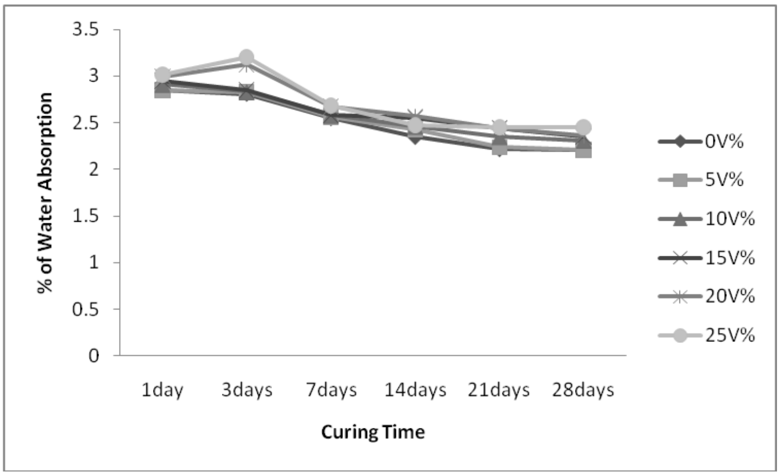


Figure 4.35: Variation of % of water absorption with number of days of curing for Polyester modified cement mortar/RPF

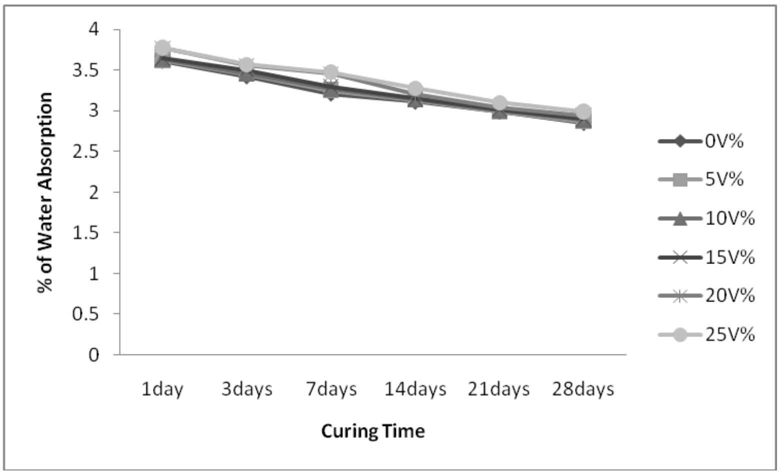


Figure 4.36: Variation of % of water absorption with number of days of curing for unmodified cement mortar/RPFAp

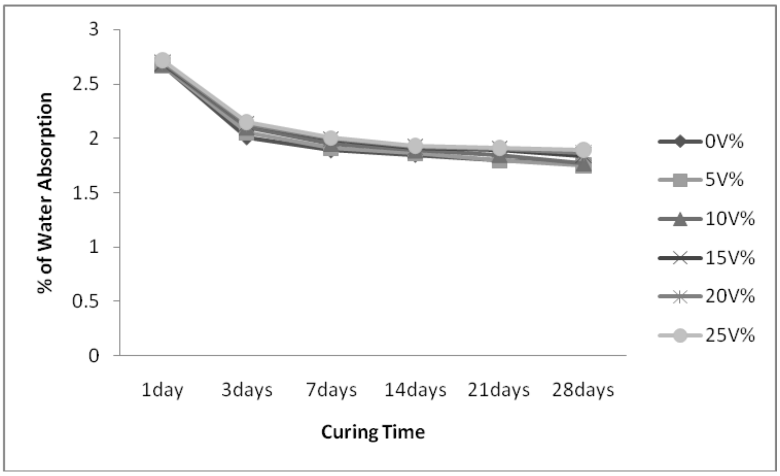


Figure 4.37: Variation of % of water absorption with number of days of curing for PVA modified cement mortar/RPFAp

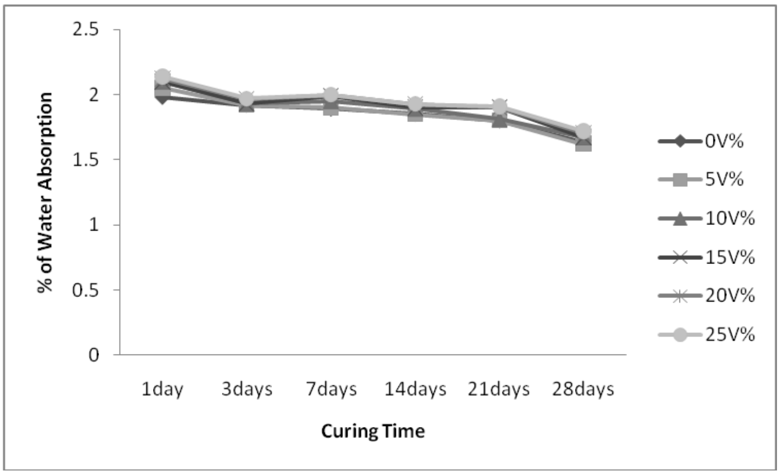


Figure 4.38: Variation of % of water absorption with number of days of curing for Polyester modified cement mortar/RPFAp

4.5 X-ray Powder Diffractometry (Xrd)

Figures 4.39-4.42 shows the XRD patterns of cement mortar composites at 2.5 volume percent of the reinforcement and Tables 4.4-4.5 showed their corresponding major phases. The particle size of the cement mortar composites has been calculated employing the Scherres equation (Aigbodion and Hassan, 2010):

$$D=\frac{K\lambda}{\beta Cos\theta} \quad (4.3)$$

Where θ is the angle between the incident and diffracted beams (degree), β the full with half maximum (rad.), D the particle size of the sample (nm), and λ the is wavelength of the X-ray.

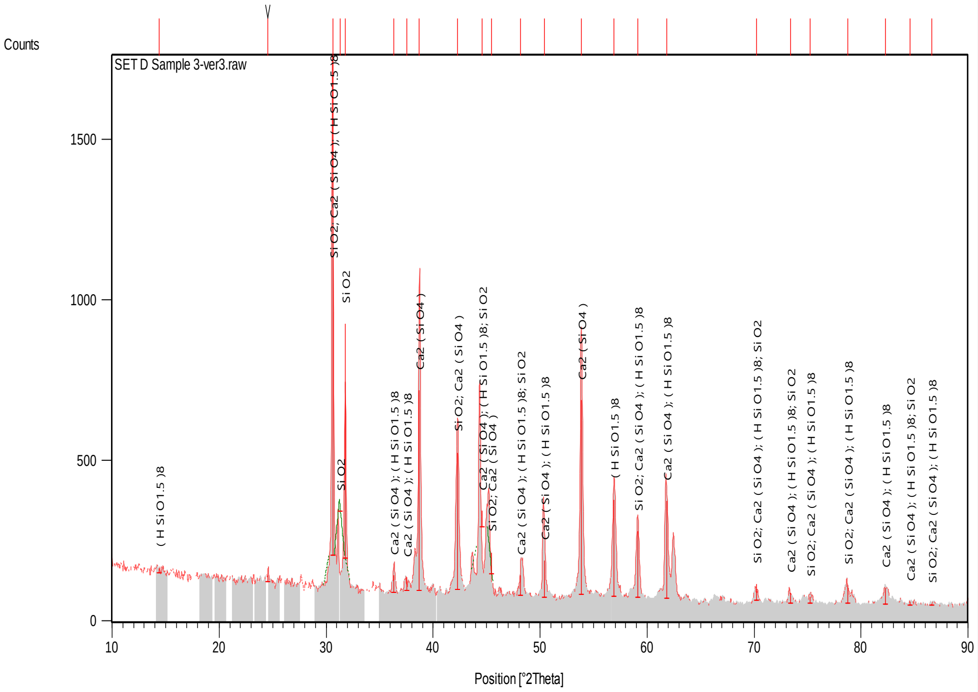


Figure 4.39: XRD spectrum of the PVA modified RPF Cement mortar

Table 4.4: Identified peaks of the PVA modified RPF Cement mortar

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	74-0765	37	Silicon Oxide	0.000	0.959	$Si\ O_2$
*	86-0399	22	Calcium Silicate	0.000	0.208	$Ca2\ (\ Si\ O_4\ )$
*	74-1377	8	Hydrogen Silicate	0.000	0.032	$(\ H\ Si\ O1._5\ )8$
*	81-0066	36	Silicon Oxide	0.000	0.344	Si O2

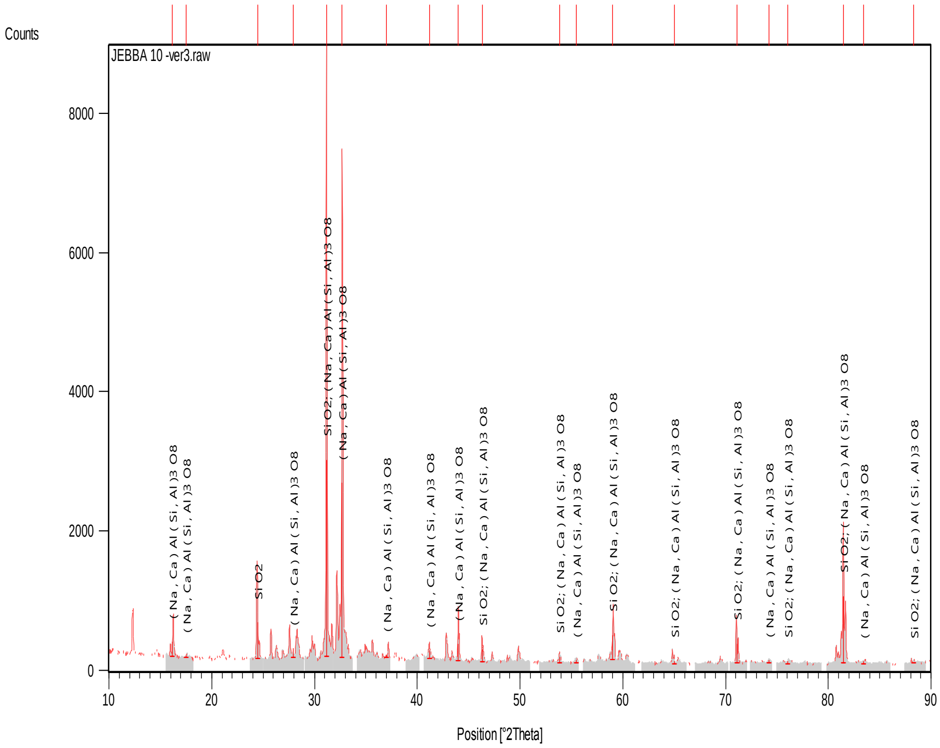


Figure 4.40: XRD spectrum of the polyester modified RPF Cement mortar

Table 4.5: Identified peaks of the polyester modified RPF cement mortar

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	85-0794	67	Silicon Oxide	0.000	0.346	Si O2
*	41-1480	40	Albite, Ca-rich, ordered	0.000	0.257	(Na , Ca) Al (Si , Al)3 O8

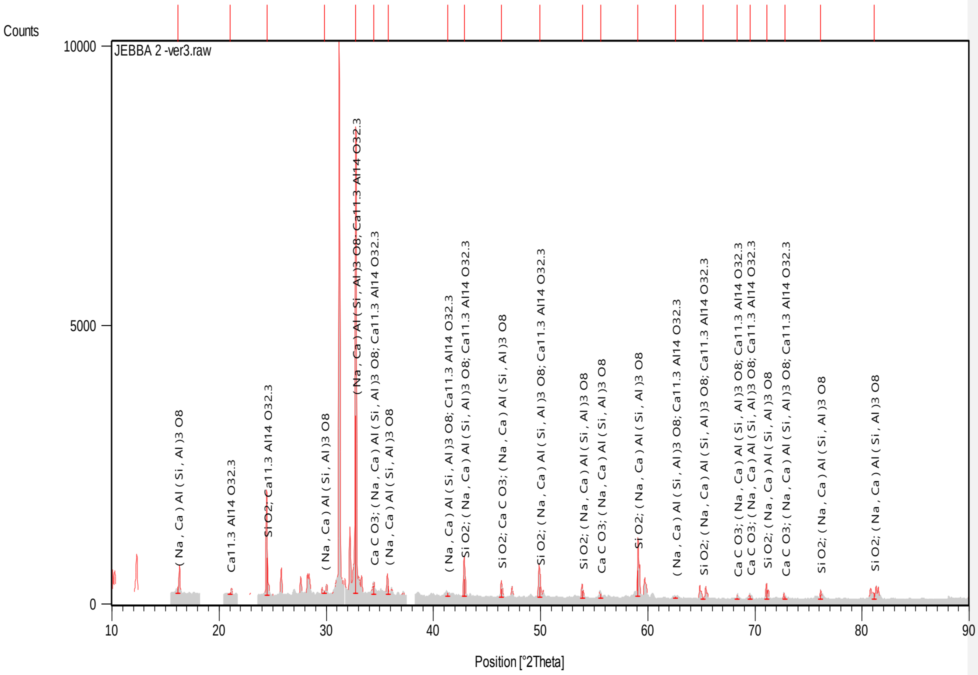


Figure 4.41: XRD spectrum of the PVA modified RPFAp cement mortar

Table 4.6: Identified peaks of the PVA modified RPFAp Cement mortar

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	03-0427	44	Quartz	0.000	0.034	$Si O_2$
*	85-0849	43	Calcium Carbonate	0.000	0.016	$Ca C O_3$
*	41-1480	41	Albite, Ca-rich, ordered	0.000	0.105	$(Na , Ca) Al (Si , Al)_3 O_8$
*	78-0910	21	Mayenite, syn	0.000	0.022	$Ca_{11.3} Al_{14} O_{32.3}$

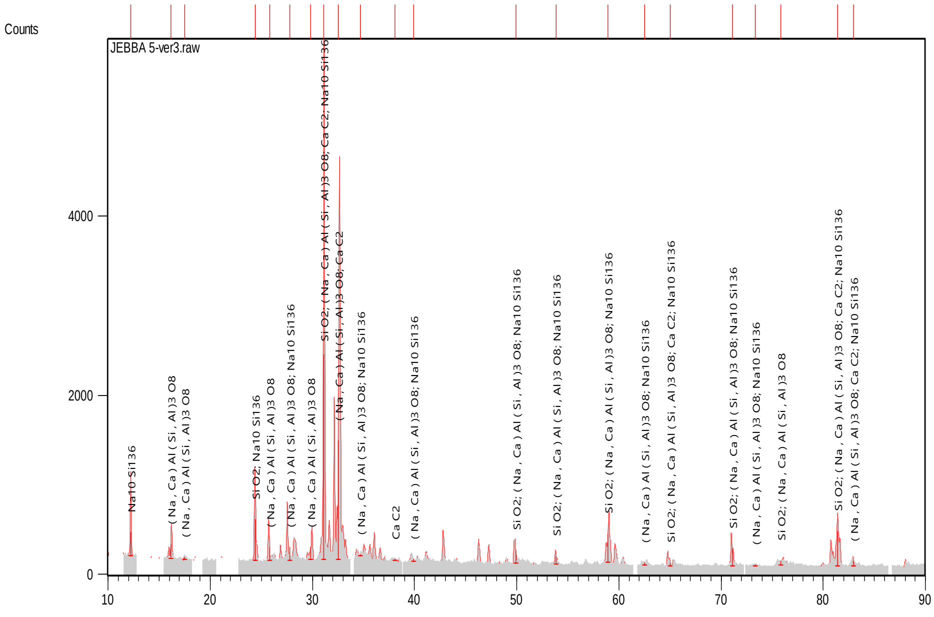


Figure 4.42: XRD spectrum of the polyester modified RPFAp Cement mortar

Table 4.7: Identified peaks of the polyester modified RPFAp cement mortar

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	86-1629	74	Quartz low	0.000	0.638	Si O2
*	41-1480	47	Albite, Ca-rich, ordered	0.000	0.493	(Na , Ca) Al (Si , Al)3 O8
*	01-1028	30	Calcium Carbide	0.000	0.239	Ca C2
*	74-0084	26	Sodium Silicon	0.000	0.014	Na10 Si136

The mechanical behaviour of a fibre/particles-cement composite is directly related to the bond between fibre/particles and cement matrix. This bond depends on many factors like the physical characteristics of the fibres/particles: geometry, type, surface characteristics, orientation, volume and distribution, the chemical composition of the fibre/particles, but also the treatment of the fibre/particles and additives in the cement mixture. Since cement is an alkaline inorganic material containing surface hydroxyl groups (Ca-OH, Si-OH and Al-OH) and Raffia palm fibres contain covalent hydroxyl groups (C-OH) from either residual lignin or the cellulose component and the oxidation of end groups and the sand which contains SiO_2 and Al_2O_3, since the composites have been cured in wet conditions the hydrogen bonds are broken by insertion of water molecules between the covalent bonds.

The major phases observed in this work are: Calcium Silicate, Silicon Oxide, Albite, Ca-rich, ordered, Calcium Carbide, Mayenite, syn, Calcium Carbonate ($C_{35} H_{25} N_3 O_6$)n, $C_{11} H_{11} N O$); these phases showed that there are interfacial reaction between the sand, cement and the Raffia palm fibres/particles. The Calcium Silicate has the higher peaks, while there is presence of Calcium Carbide in the RPFAp cement mortar due to the carbonization of the RPF, Silica oxide (SiO_2) peak indicated free silica present in cement mixes. The phases obtained in this present work are on a par with the results of other researches in this area (Chandra et al, 1994; Fowler, 1989).

Also it can be observed that the interspacing distance of the RPFAp cement mortar are closer than the RPF cement mortar (compare Figures 4.39-4.40 with Figures 4.41-4.42): that means there are more peaks in the RPFAp composites than that of the RPF composites. This supported the earlier claim that the RPFAp composites have low water absorption than that of the RPF composites. The complete mineralization analysis revealed that the composites contain at least one of: elements = "H, C, N, O, Al, Si, Ca, C, K, Na O,"

4.6 Compressive Strength

The results of the compressive strength are showed in Figures 4.43-4.48 and Tables A10-A11 (Appendix A). From the results, it can be observed that the compressive strength increases with increasing number of days of curing. This can be attributed to proper strong bond form as the number of days of curing is increasing. Also the compressive strength of RPFAp cement mortar increased as the volume percent of RPFAp increased in the formulation (see Figures 4.43-4.45), while the compressive strength of the RPF decreased as the volume percent increased in the formulation (see Figures 4.46-4.48). The lower compressive strength of the cement mortar prepared with the RPF might be due to the following reasons. 1) The presence of a weaker fibrous matrix in the cement might also disrupt the continuity of the cement matrix and hence loads paths. A longitudinal compressive loading would set up lateral tensile stresses, and hence lower ultimate compressive strength inversely proportional to the fibre content was observed. 2) Insufficient dispersing of the fibres occurred in the cement during mixing. These micro fibres that failed to disperse fully in the cement mortar tend to form a multifilament structure.

Compressive strengths in the case of PVA are much higher than that of polyester-based samples. This can be attributed to a greater probability of chemical interaction between PVA and cement. Polyester has only limited possibility for interaction with cement due to the ester structure of polyester. Also the increase in the compressive strength of the RPFAp composites can be attributed to increase in the surface area of the particles which results to increase in the numbers of peaks in the RPFAp as evident in the XRD spectrum above.

Comment [Kingsley20]: Something is missing here.

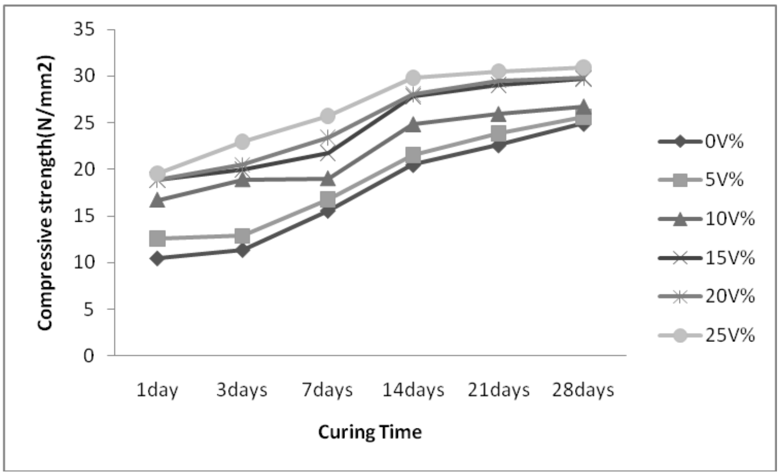


Figure 4.43: Variation of Compressive strength with number of days of curing for unmodified cement mortar/RPFAp

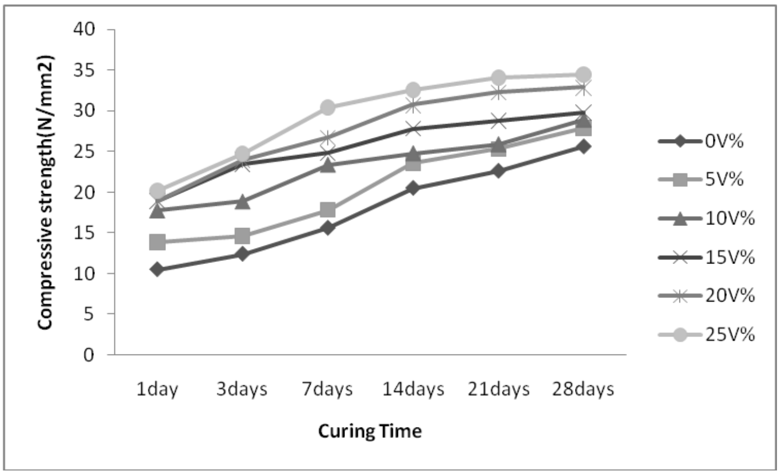


Figure 4.44: Variation of compressive strength with number of days of curing for polyester modified cement mortar/RPFAp

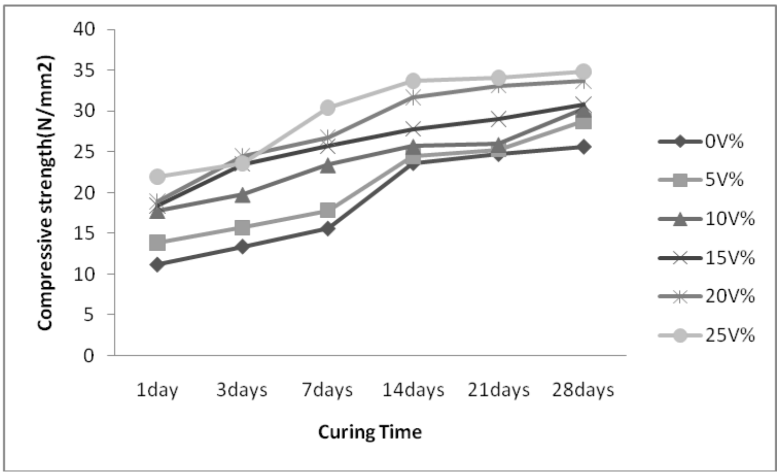


Figure 4.45: Variation of compressive strength with number of days of curing for PVA modified cement mortar/RPFAp

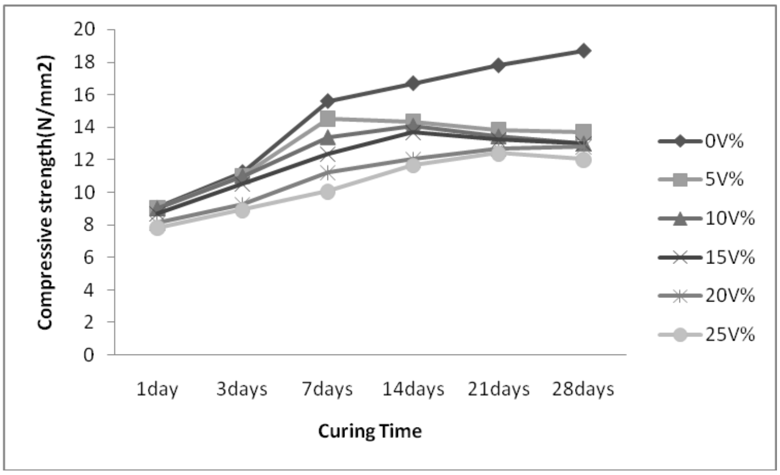


Figure 4.46: Variation of compressive strength with number of days of curing for unmodified cement mortar/RPF

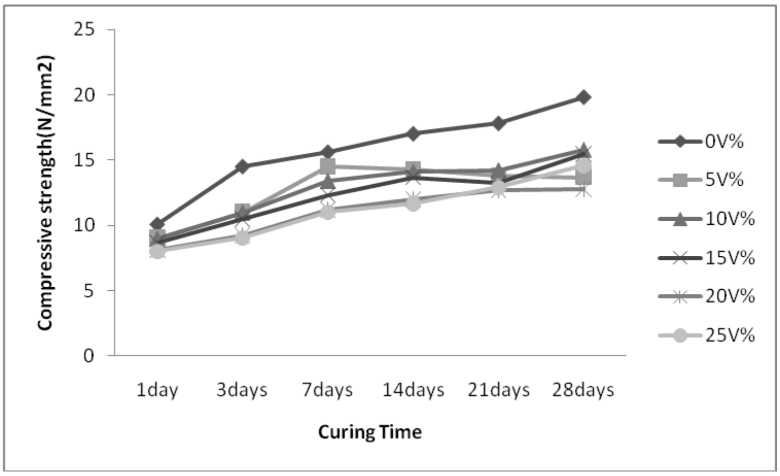


Figure 4.47: Variation of compressive strength with number of days of curing for polyester modified cement mortar/RPF

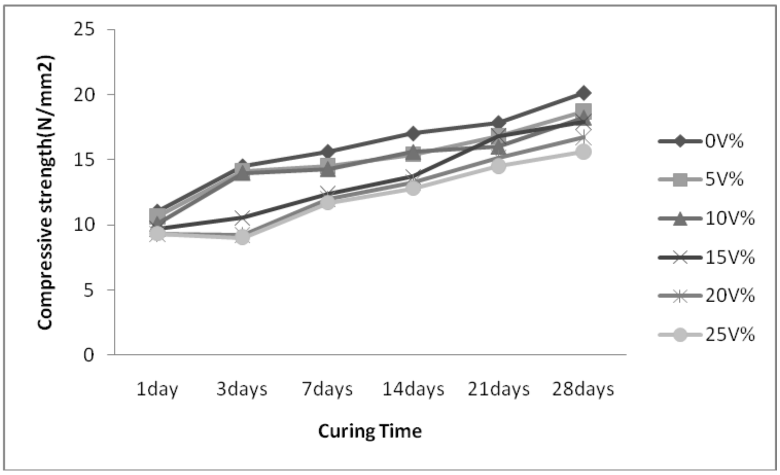


Figure 4.48: Variation of compressive strength with number of days of curing for PVA modified cement mortar/RPF

4.7 Microstructure

The SEM/EDS microstructure of the fracture surface from the compressive test is shown in Figures 4.49-4.54.

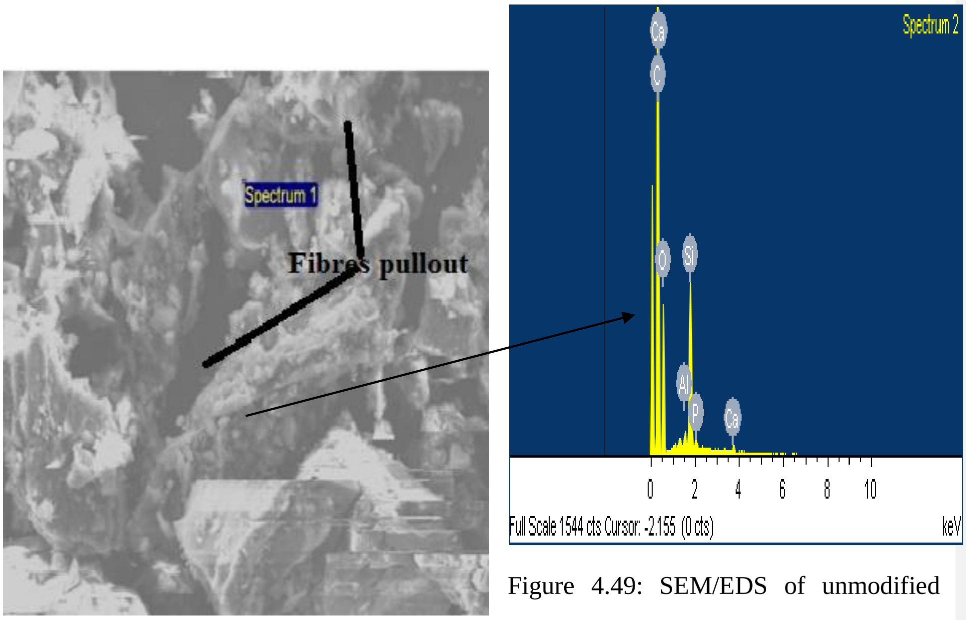


Figure 4.49: SEM/EDS of unmodified RPF cement mortar composites

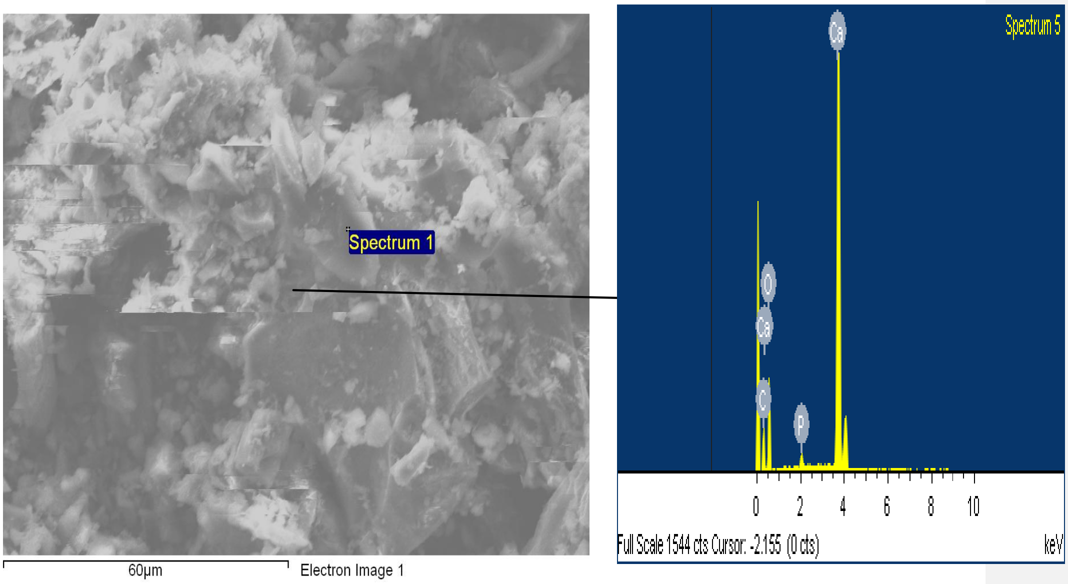


Figure 4.50: SEM/EDS of unmodified RPFAp cement mortar composites

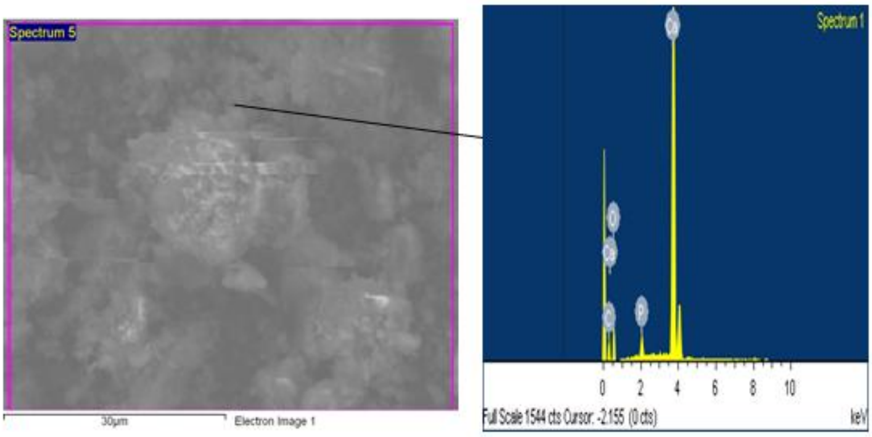


Figure 4.51: SEM/EDS of polyester modified RPF cement mortar composites

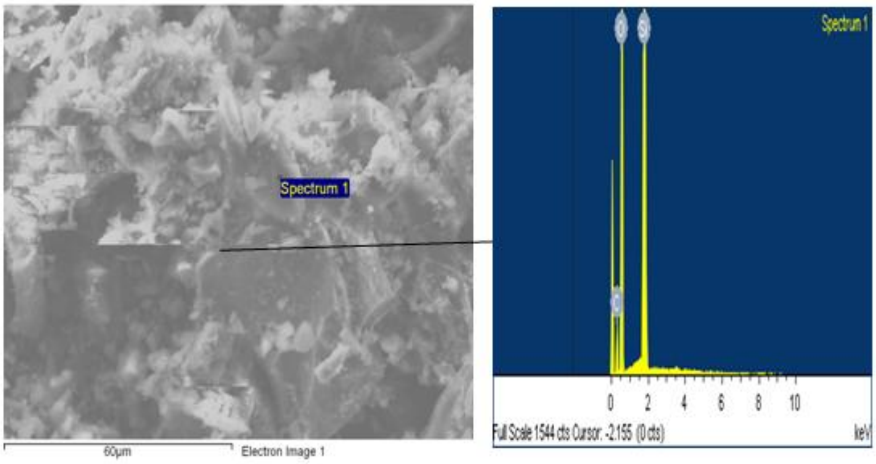


Figure 4.52: SEM/EDS of modified RPFAp cement mortar composites polyester

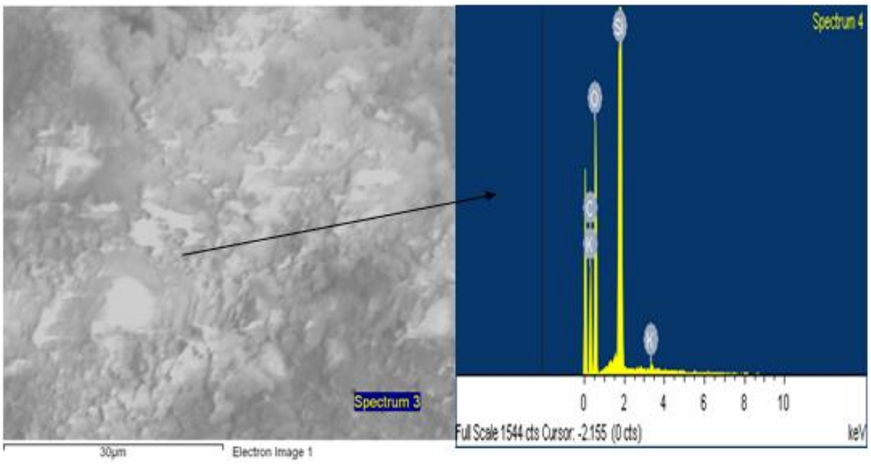


Figure 4.53: SEM/EDS of PVA modified RPF cement mortar composites

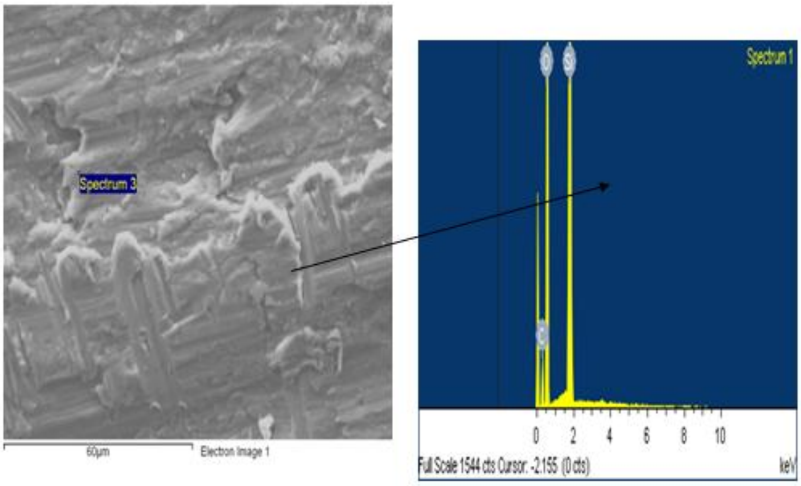


Figure 4.54: SEM/EDS of PVA modified RPFAp cement mortar composites

In images of tested fibres/particles done in the SEM patches of cement matrix covering the fibres/particles have been observed (Figures 4.49-4.54). Those patches are these thin layers of reacted paste. SEM images of the polymer-modified samples reveal a sound and intimate contact between the fibres/particles and cement matrix as presented in Figures 4.51-4.54. In the SEM, under BSE mode, the polymer looks dark gray because it has a lower atomic number than the fibre/particles or the cement matrix; there is frictional behaviour during pullout if the fibres have an irregular shape, rough surface or curvature along its length. This can be seen with fibres. Even though the fibre surface is not regular, the bond with the matrix is sound in both cases.

In some segments of the interface the matrix is more porous, which may lead to lower pullout shear stress when the fibre is pulled out. In all, the SEM of cement mortar composites, the internal structure of the cement, reveals needle-like crystals of cement gel, plates and the elongated ettringite crystals, all of which are products of cement hydration. Due to these crystallized forms, cleavage sites are developed on the surfaces. The microstructure of the fracture surface of PVA cement composite in Figures 4.53-4.54 depicts a reduction in the size of the hydrated cement crystals. This has resulted in a more compact structure than unmodified cement paste and absence of microvoids in the polymer cement matrix. The layers of the polymer are seen on the cement particles and these stretch and bridge the gap between the voids and cracks. The crystallized rods of ettringite in PVA are an indication of its gradual formation due to the consumption of Ca ions by the acetate groups in the PVA. This also shows that the addition of the polymer decreases the hydration of cement by consuming the Ca ions present in the aqueous phase.

In the polyester-modified cement mortar (Figures 4.51-4.52), the polymers form a dense three-dimensional network when crosslinked and enclose the cement particles in the network. The crosslinking forms a three-dimensional network after hydration of cement particles. When the resin gets crosslinked, some of the cement particles get embedded in it. Therefore, the hydration of these cement particles does not go to the completion stage. This coherent network of the polymer in the cement matrix prevents the dissolution of cement grains when exposed to external chemicals leading to enhanced chemical resistance of the composites and slows down the permeation of gases and water into the cement matrix

4.8 Tensile Strength

The tensile strength characterization of the composites reveals that the volume percent of (RPF and RPFAp), type of polymer modifier and form of the reinforce (fibers or particles have significant effect on the tensile properties of these composites. The test results for tensile strengths are shown in Figures 4.55- 4.56, Table A12 and Figure B1-B6 (Appendix B) respectively. Tensile properties of the naturally reinforced polymer-modified cement composites depend on several factors such as the stress–strain behaviors of reinforcement and matrix phases, the volume percent, the fillers concentration and the distribution of the reinforcement.

The stress-strain curve of the composite loaded under tensile is characterized by an ascending branch up to the peak stress, followed by a descending branch. The increment of load results in a variation of internal stiffness and stress with a progressive microcrack growth. The effect of RPF on the stress-strain behaviour (see Figures B1-B3) of the matrices can be divided in two parts. In the pre-peak zone, the addition of RPF tends to reduce the peak stress and elastic modulus of the matrix. In the post-peak zone when the crack face bridging by grains fails, stress transfer over the crack is possible through fibres intersecting with the crack. Toughening in the natural fibre-reinforced composites occurs largely as a result of crack bridging. The presence of fibres in the cement reduces the unstable propagation of macrocracks and permits a ductile post-peak behaviour once the fibres can provide sufficient forces to suppress crack opening and redistribute the stresses onto the nearby matrix, thus suppressing strain localization. Therefore, the addition of RPF results in an increment of tensile strength of material (see Figure 4.55). This indicates that addition of RPF filler improves the load-bearing capacity of the composites. While in the RPFAp, the reverse is the case, adding RPFAp in particulate form in the cement mortar decreased the tensile strength. Also after the ultimate tension, the decrease in measured stress with increase in deformations was much less in RPFAp than in samples with RPF. As a result the RPF composites have large area under the stress-strain curve than RPFAp composites. However the tensile obtained for the RPF is within the acceptable limit for roofing sheets

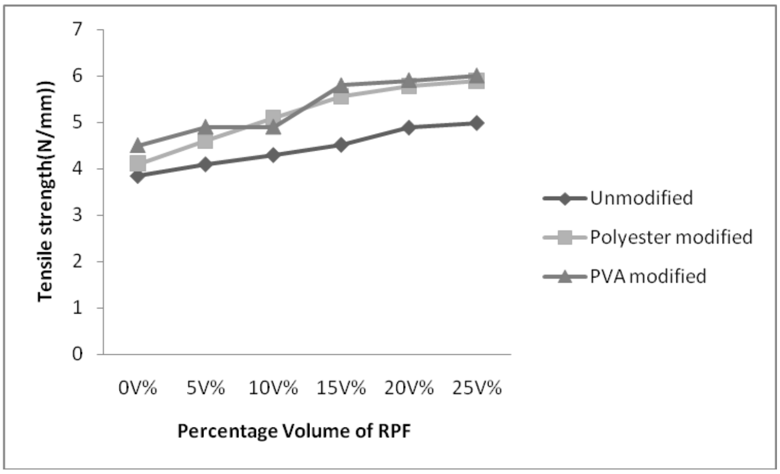


Figure 4.55: Tensile strength of RPF cement mortar composites

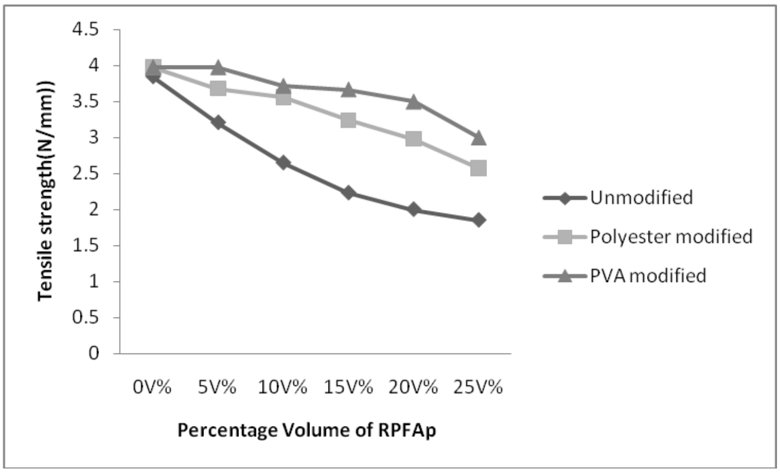


Figure 4.56: Tensile strength of RPFAp cement mortar composites

4.9 Flexural Strength

This is one of the very important properties of a mortar for roofing sheets application. The results of the flexural strength are shown in Figures 4.57-4.4.58 and Table A13 (Appendix A). From Figure 4.57-4.58, it can be observed that the flexural strength of the RPF mortar rises as the volume percentage of the RPF increased in the mortar. For the RPFAp mortar increasing the RPFAp content increases the flexural strength of the composite, but beyond a certain limit of 1.5%vf the strength decreases. However the results have a similar trend to that of the tensile strength, which also confirmed that the flexural strength of the RPF composites mortar is higher than that of the RPFAp composites mortar; this is expected because the RPF inside the mortar helps to increase the load-bearing capacity and stiffness of the cement mortar.

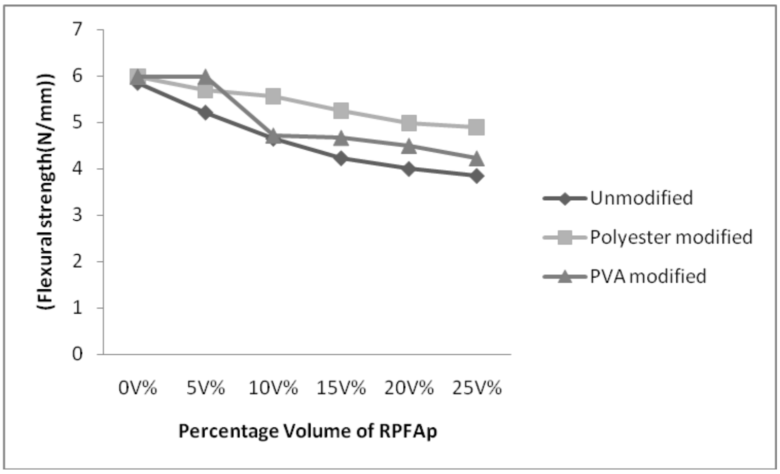


Figure 4.57: Flexural Strengthof RPFAp cement mortar composites

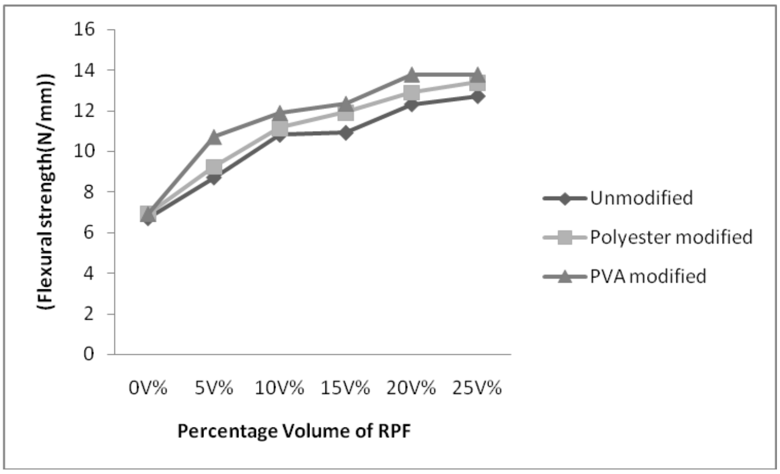


Figure 4.58: Flexural strengthof RPF cement mortar composites

4.10 Impact Energy

The results of the impact energy in Figures 4.59-4.60 and Table 14 (Appendix A) show that the impact energy of the RPFApcomposites slightly decreased with increase in RFPA addition while that of RPF rises as the RPF increased in the cement mortar. High strain rates or impact loads may be expected in many engineering applications of composite materials. The suitability of a composite for such applications should therefore be determined not only by usual design parameters, but by its impact or energy absorbing.

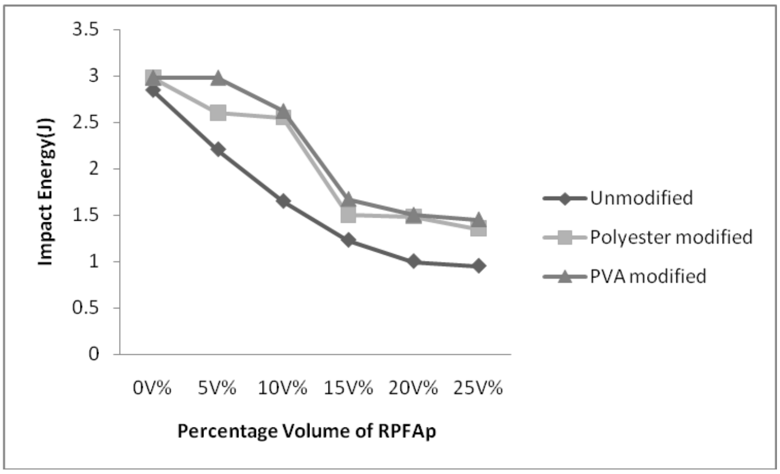


Figure 4.59: Impact energy of RPFAp cement mortar composites

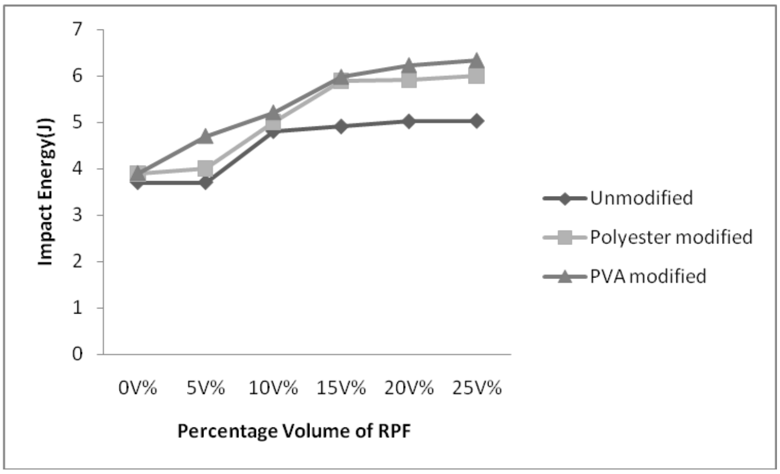


Figure 4.60: Impact energy of RPF cement mortar composites

The steep reduction in the impact energy of the RPFAp composites could be attributed to the presence of particle clusters and weight fraction of second phase particles. These factors contribute to decrease in weight fraction of the ductile phase (weight fraction of the matrix phase), and thereby leads to decrease in impact energy. Also it is obvious that plastic deformation of the mixed cement matrix and the non-deformable reinforcement is more difficult than the cement matrix. These results are in agreement with the work of other researchers (Bahadur et al, 1993; Ettu et al, 2013; Eze-Uzomaka et al, 1990).

The reduction in impact energy and energy with increasing RPFAp filler loading might also be due to the decreased deformability of a rigid interface between the filler and cement matrix. At similar filler loading, composites with RPFAp indicate lower impact energy than composites of RPF. Composites with RPF have increased the tensile strength of composites, with an enhancement in the rigidity and improvement of the toughness of composites, which consequently increased the impact energy of the composites. This phenomenon can be observed on the stress-strain curves in Figures B1-B6. This is a clear indication that the RPF composites have a large area under the stress-strain curves than RPFAp composites (compared Figures B1-B3 to B4-B6). However the results obtained remained within the standard level for roofing sheets applications (Bahadur et al, 1993; Ettu et al, 2013).

4.11 Thermal Properties

The temperatures of destruction (T_{des}) of the cement matrix and the composites, subjected to investigation, were determined from DTA curves. DTA data were recorded on "Derivatograph OD 102", at heating rate of 20°C/min in argon. The results of the DTA/TGA scan of the cement matrix and that of the composites are shown in Figures 4.61-4.64. The result indicates that the composites with RPFAp biomass show less percentage of decomposition (see Figures 4.63-4.64). At temperature above 500°C, the residual weight stabilized, which agrees with the silica and carbon content in RPFAp, and this is on a par with what was earlier reported in literature (Capart et al, 2004). As the samples were heated close to 450°C, it started to decompose and the decomposed byproducts, including silica and carbon were, formed. The silica ash gradually accumulated on the cement matrix which delays the degradation process and makes the cement more thermally stable.

The maximums of the endothermic peaks shift to higher temperature after the increase of weight of the RPFAp which reflects the improved thermal stability of cement matrix due to incorporation of RPFAp, but shift to a lower temperature with RPF. It was established that the RPFAp addition cement mortar enhances the stabilizing and increases the temperature of the maximal decomposition/destruction rate. From the thermal analysis results it was clear that the RPFAp composites still retailed above 80% of its weight at temperature around 900°C. While that of RPF composites still retailed above 9% of its weight at temperature around 900°C. However, the results obtained are within the standard values for roofing sheets.

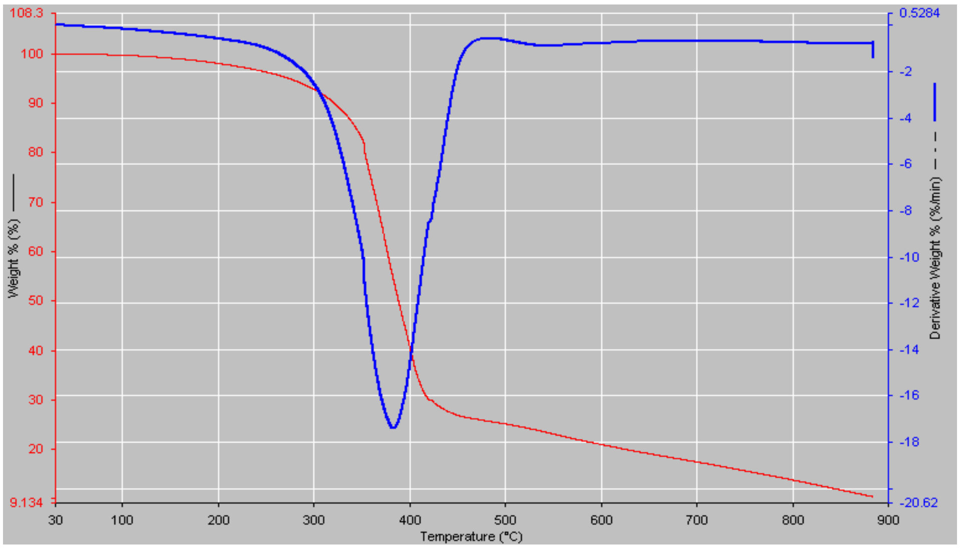


Figure 4.61: DTA/TGA analysis of 20V% RPF composites(PVA)

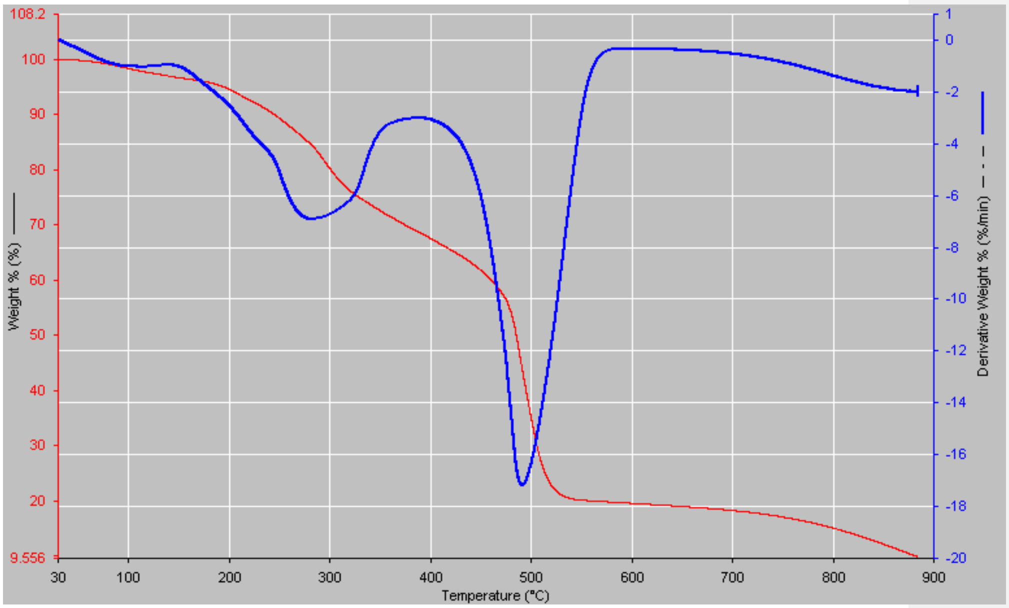


Figure 4.62: DTA/TGA analysis of 20V% RPF composites (Polyester)

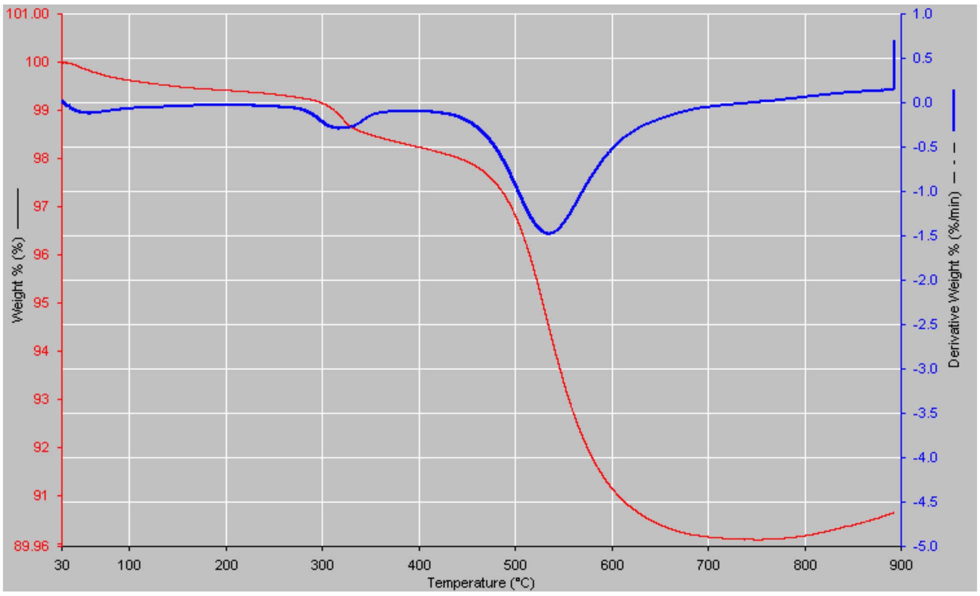


Figure 4.63: DTA/TGA analysis of 20V% RPFAp composites(Polyester)

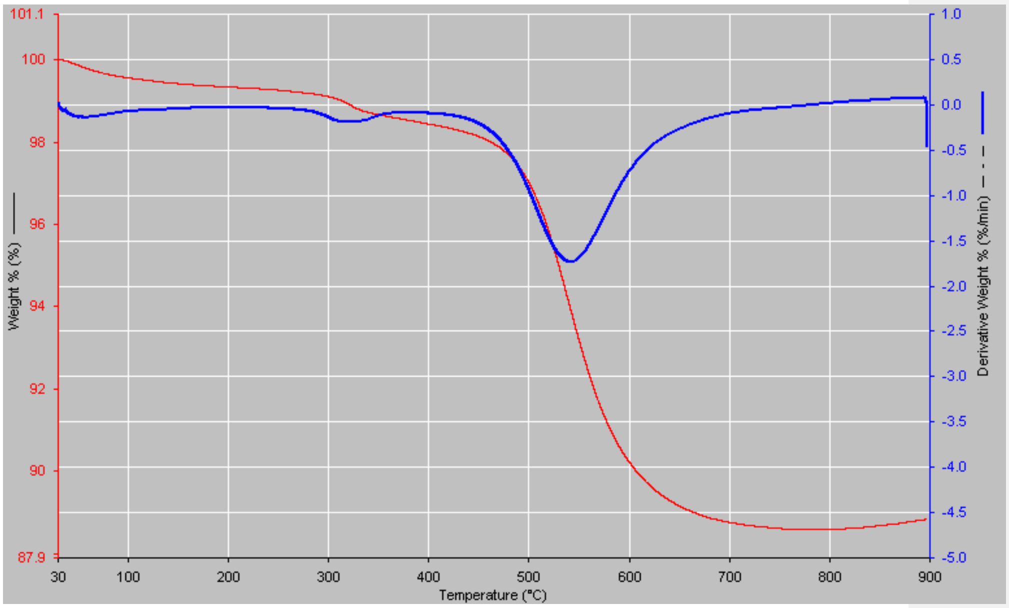


Figure 4.64: DTA/TGA analysis of 20V% RPFAp composites (PVA)

4.12 Model for Prediction of the Compressive Strength and Water Absorption of the Cement Mortar

The standard order of sequence as shown in Table 4.8, the sum of squares for main and interaction effects was calculated using Yates algorithm. The significant factors (main and interaction) were identified by analysis of variance technique.

Table 4.8: Standard Order of Test Sequence and Result

Exp.number	Sample condition(A)	Volume %(B)	Curing time(C) days
1	Umodified(-1)	0.0(-1)	1(-1)
2	Modified(+1)	0.0(-1)	1(-1)
3	Umodified(-1)	25(+1)	1(-1)
4	modified(+1)	25(+1)	1(-1)
5	Umodified(-1)	0.0(-1)	28(+1)
6	modified(+1)	0.0(-1)	28(+1)
7	Umodified(-1)	25(+1)	28(+1)
8	modified(+1)	25(+1)	28(+1)

4.12.1 Statistical Design and Modeling of the % Water Absorption

The results of the experiment are shown in Tables 4.9-4.10 for the RPF and RPFAp cement mortar resepectively.

Table4.9: Expanded plan matrix for factorial design of the RPF cement mortar (%water absorption)

S/n	x_0	A	B	C	AB	AC	BC	ABC	%Water absorptio	
									PVA	Polyester
1	1	-1	-1	-1	+1	+1	+1	-1	4.13	4.13
2	1	1	-1	-1	-1	-1	+1	+1	3.01	2.85
3	1	-1	1	-1	-1	1	-1	+1	4.52	4.52
4	1	+1	+1	-1	+1	-1	-1	-1	3.29	3.01
5	1	-1	-1	+1	+1	-1	-1	+1	3.34	3.34
6	1	+1	-1	+1	-1	+1	-1	-1	2.34	2.21
7	1	-1	+1	+1	-1	-1	+1	-1	4.28	4.280
8	1	1	1	1	1	1	1	1	2.61	2.45
Effects(PVA)	3.44	-1.255	0.47	-0.595	-0.008	0.135	0.135	-0.14		
Effects(Polyester)	3.35	-1.438	0.4325	-0.558	-.0.233	-0.042	0.158	-0.12		

Table4.10: Expanded plan matrix for factorial design of the RPFAp cement mortar (%water absorption)

S/n	x_0	A	B	C	AB	AC	BC	ABC	%Water absorption	
									PVA	Polyester
1	1	-1	-1	-1	+1	+1	+1	-1	3.61	3.61
2	1	1	-1	-1	-1	-1	+1	+1	2.67	1.98
3	1	-1	1	-1	-1	1	-1	+1	3.78	3.78
4	1	+1	+1	-1	+1	-1	-1	-1	2.72	2.14
5	1	-1	-1	+1	+1	-1	-1	+1	2.85	2.85
6	1	+1	-1	+1	-1	+1	-1	-1	1.77	1.63
7	1	-1	+1	+1	-1	-1	+1	-1	2.99	2.99
8	1	1	1	1	1	1	1	1	1.89	1.72
Effects(PVA)	2.79	-1.05	0.12	-0.82	-0.017	-0.045	0.01	0.025		
Effects(Polyester)	2.59	-1.44	0.13	-0.58	-0.015	0.195	-0.025	-0.01		

From the result of factorial design in Tables 4.9-4.10, the % wt of sample condition appears to be the most important variable with main effect of (-1.255, -1.438) and (-1.05, -1.44) for the RPF and RPFAp composites respectively. These mean that using PVA-modified reduced the % of water absorption by -1.255 and -1.05 for RPF and RPFAp composites respectively. Also using polyester-modified reduced the % of water absorption by -1.438 and -1.44 for RPF and RPFAp composites respectively. It can also be seen that polyester-modified cement mortar have undergone minimum water absorption. This may be due to the sealing of the pores and voids by the polymer which possibly prevents the entry of water into the polymer cement matrix, thereby inhibiting water interactions. The effects of volume percent of RPF and RPFAp composites mortar are positive, that means increasing the volume percent from 0 to 25V% increased the water absorption, and the effects of curing time of the composites are negative – meaning that increasing the curing time from 1 to 28 days decreased that water absorption. This is attributed to rate of hydration which is high in the initial period but decreases with time, which leads to decrease in % of water absorption. Design-expert software was also used to verify these effects (see Figures 4.65-4.72). Figures 4.65-4.72 shows the estimated response surface for water absorption as a function of sample condition, volume percent and curing time. It can be seen that the water absorption of both was highly influenced by the sample condition (A) and curing time (C), for the sample condition and curing time were found to decreased when changing sample condition from umodified to modified and curing time from 1 to 28 days. Also the volume percent of RPF (B) raise from 0.0 to 25V% water absorption increased (see Figures 4.65-4.72).

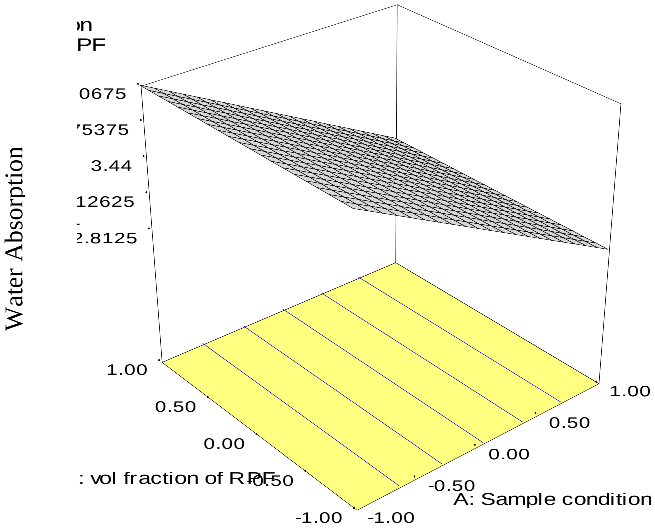


Figure 4.65: 3D surface plot of the effect of water absorption for RPF mortar (PVA)

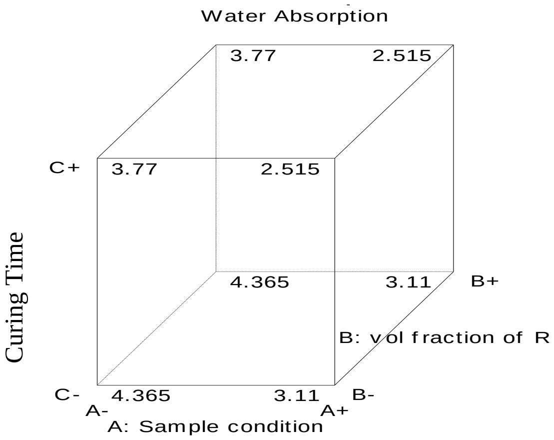


Figure 4.66: Cube plot of the effect of water absorption for RPF mortar(PVA)

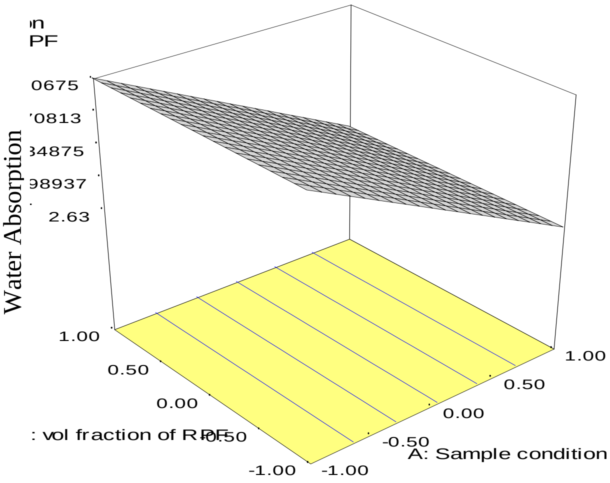


Figure 4.67: 3D surface plot of the effect of water absorption for RPF mortar(Polyester)

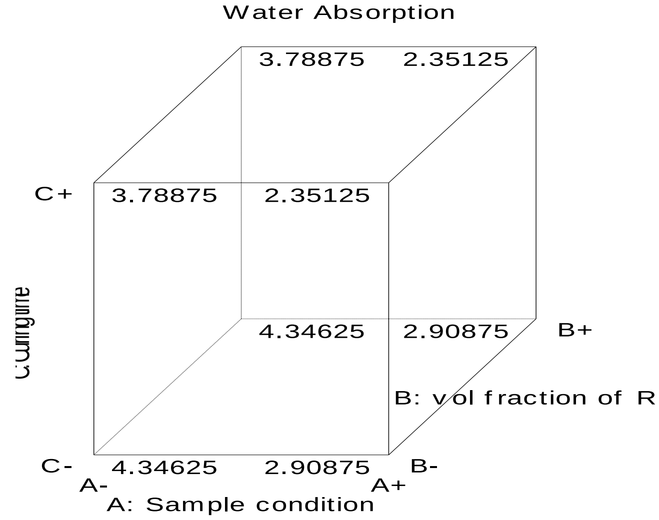


Figure 4.68: Cube plot of the effect of water absorption for RPF mortar (Polyester)

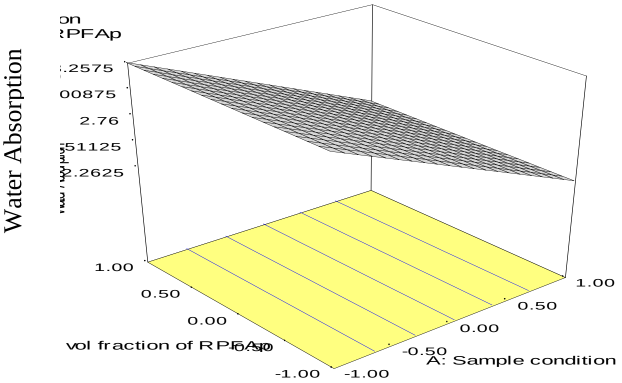


Figure 4.69: 3D surface plot of the effect of water absorption for RPFAp mortar (PVA)

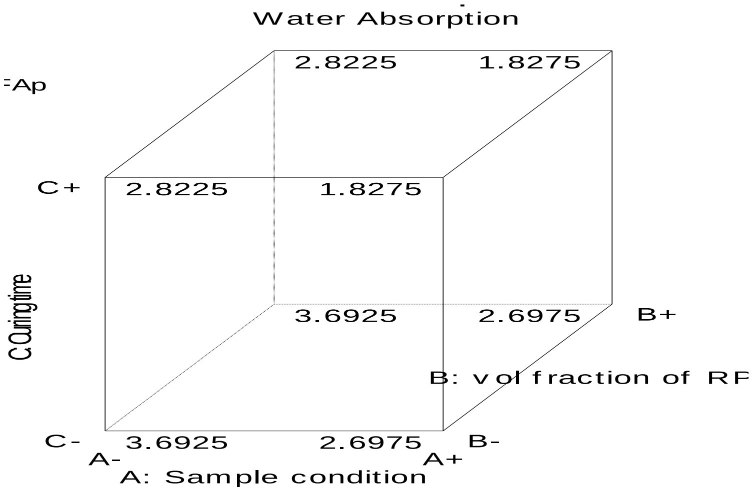


Figure 4.70: Cube plot of the effect of water absorption for RPFAp mortar (PVA)

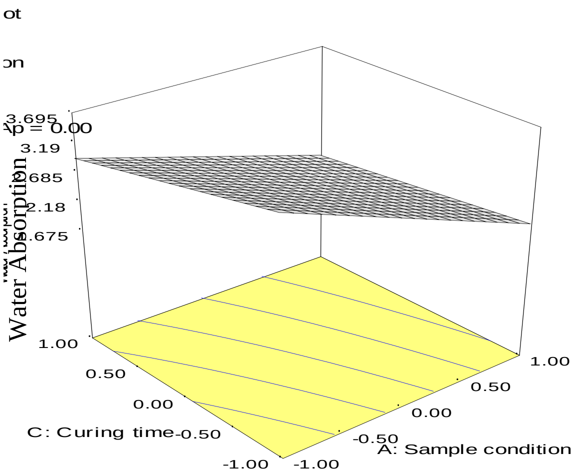


Figure 4.71: 3D surface plot of the effect of water absorption for RPFAp mortar (Polyester)

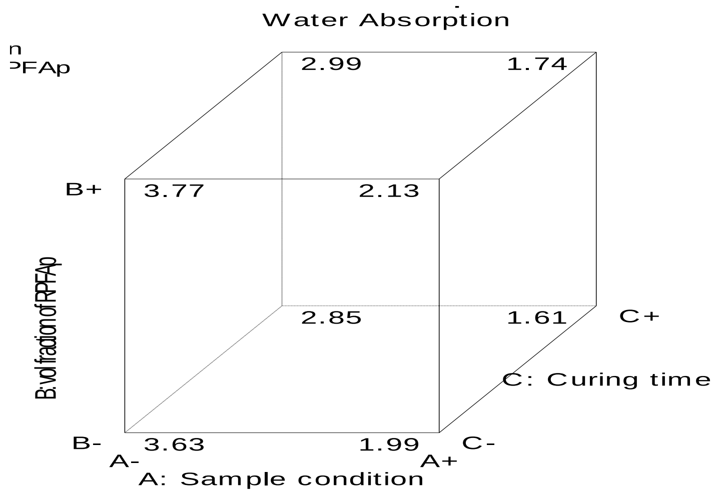


Figure 4.72: Cube plot of the effect of water absorption for RPFAp mortar (Polyester)

ANOVA was used to determine the design parameters significantly influencing the water absorption. The values of F calculated (F=Fishers distribution) were compared with *F* critical. *F* distribution critical values for degrees of freedom (1, 7) at 95% confidence level (see Table 4.11). For the ANOVA of RPF cement composites (PVA), it was observed that the Model F-value of 34.85 implies that the model is significant. There is only a 0.25% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case A(sample condition), B(volume % of RPF), C(curing time) are significant model terms(see Table 4.11). The "Pred R-Squared" of 0.8526 is in reasonable agreement with the "Adj R-Squared" of 0.9355 with a standard devation of 0.2 and mean of 3.44.

The developed model equation for the water absorption of RPF cement composites(PVA) can be expressed as: $W_{PVA}=+3.44-0.63A + 0.24B - 0.30C + 0.022AB$ (4.1)

Also substituting the coded values of the variables for any experimental condition in Equation 4.1, the water absorption for the RPF cement composites (PVA) can be calculated. Figure 4.73 shows the predicted values along with the actual experimental values in different experimental conditions.

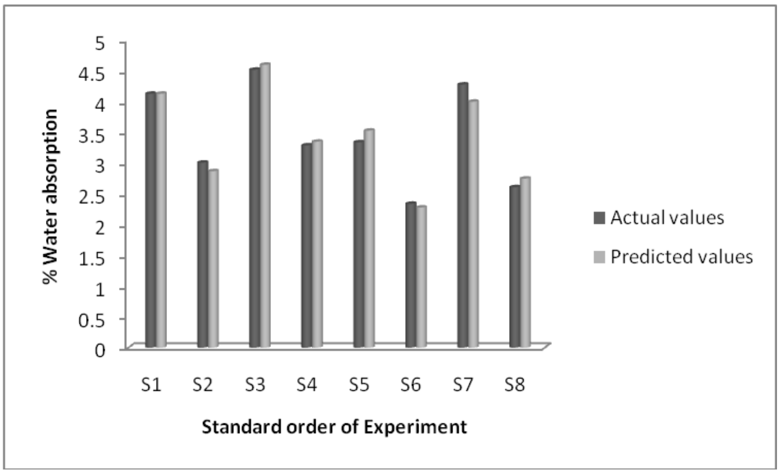


Figure 4.73: Variation of the % water absorption with Experimental Numbers for the RPF cement composites (PVA)

For the ANOVA of RPF cement composites (polyester), it was observed that the Model F-value of 21.11 implies that the model is significant. There is only a 0.36% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case A(sample condition) is significant model terms (see Table 4.11). The "Pred R-Squared" of 0.7289 is in reasonable agreement with the "Adj R-Squared" of 0.8518. with a standard devation of 0.35 and mean of 3.45.

Table 4.11: ANOVA for selected factorial model of the water absorption (RPF composites)

		%Water absorption for RPF composites (PVA)				
Source	Sum of Squares	DF	Mean square	F_{value}	P_{value}	Remarks
Model	4.30	3	1.43	34.88	0.0025	Significant
A	3.15	1	3.15	76.83	*0.0009*	Significant
B	0.44	1	0.44	10.73	*0.0306*	Significant
C	0.708	1	0.708	17.27	*0.0143*	Significant
AB	0.0761	1	0.0761	1.855	0.0456	Significant
AC	0.0128	1	0.0128	0.312	0.123	Not Significant
BC	0.0365	1	0.0365	0.89	0.134	Not Significant
ABC	0.0392	1	0.0392	0.956	0.156	Not Significant
Residual	0.165	4	0.041			
CorTotal	4.465	7				
		%Water absorption for RPF composites(Polyester)				
Model	4.75	2	2.34	21.11	0.0036	Significant
A	4.13	1	4.13	36.70	*0.0018*	Significant
B	0.374	1	0.374	3.40	*0.0556*	Significant
C	0.622	1	0.622	5.52	0.038	Significant
AB	0.108	1	0.108	0.982	0.079	Not Significant
AC	0.036	1	0.036	0.33	0.152	Not Significant
BC	1.89	1	1.89	0.50	0.123	Not Significant
ABC	0.0276	1	0.0276	0.25	0.157	Not Significant
Residual	0.56	5	0.11			
CorTotal	5.32	7				

Again the developed model equation for the water absorption of RPF cement composites (polyester) can be expressed as:

$$W_{PE}=+3.35 - 0.72A - 1.25B + 0.28C \qquad (4.2)$$

Again substituting the coded values of the variables for any experimental condition in Equation 4.2, the water absorption for the RPF cement composites (polyester) can be calculated. Figure 4.74 can be obtained. It is also evident from Figures 4.73-4.74 that the actual experimental values are also in close proximity with the predicted values.

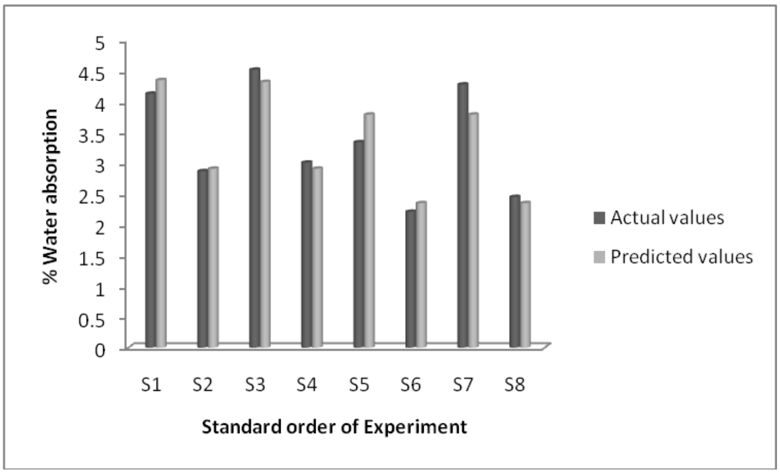


Figure 4.74: Variation of the % water absorption with Experimental Numbers for the RPF cement composites (polyester)

Table 4.12 shows the ANOVA of the model of the water absorption of the RPFAp composites. For the ANOVA of RPFAp cement composites (PVA), it was observed that the Model F-value of 352.91 implies that the model is significant. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case A(sample condition), C(curing time) are significant model terms (see Table 4.12). The "Pred R-Squared" of 0.9820 is in reasonable agreement with the "Adj R-Squared" of 0.9902 with a standard devation of 0.07 and mean of 2.76. The developed model equation for the water absorption of RPFAp cement composites (PVA) was expressed as:

$$W_{Ap\ (PVA)} = 2.76\text{-}0.50A - 0.23B - 0.44C + 0.091BC \qquad (4.3)$$

Substituting the coded values of the variables for any experimental condition in Equation 4.3, the water absorption for the RPFAp cement composites (PVA) can be calculated: Figure 4.75 can be obtained.

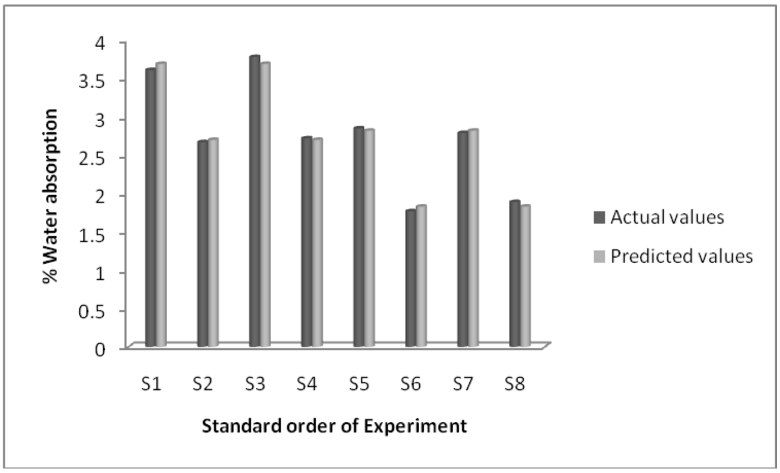


Figure 4.75: Variation of the % water absorption with experimental numbers for the RPFAp cement composites (PVA)

The Model F-value of 1948.13 implies that the model is significant. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case A (sample condition), B (volume percent of RPFAp), C (curing time), AC (interaction between sample condition and curing time) are significant model terms. The "Pred R-Squared" of 0.9973 is in reasonable agreement with the "Adj R-Squared" of 0.9991 with a standard devation of 0.025 and mean of 2.59 (see Table 4.12). The developed model equation for the water absorption of RPFAp cement composites (Polyester) was expressed as:

$$W_{Ap\ (PE)} = 2.59 - 0.72\ A + 0.070B - 0.29C + 0.098AC \qquad (4.4)$$

Substituting the coded values of the variables for any experimental condition in Equation 4.4, the water absorption for the RPFAp cement composites (polyester) can be calculated: Figure 4.76 can be obtained. Also from Figures 4.75-4.76, it was clear that the actual experimental values are also in very close proximity with the predicted values

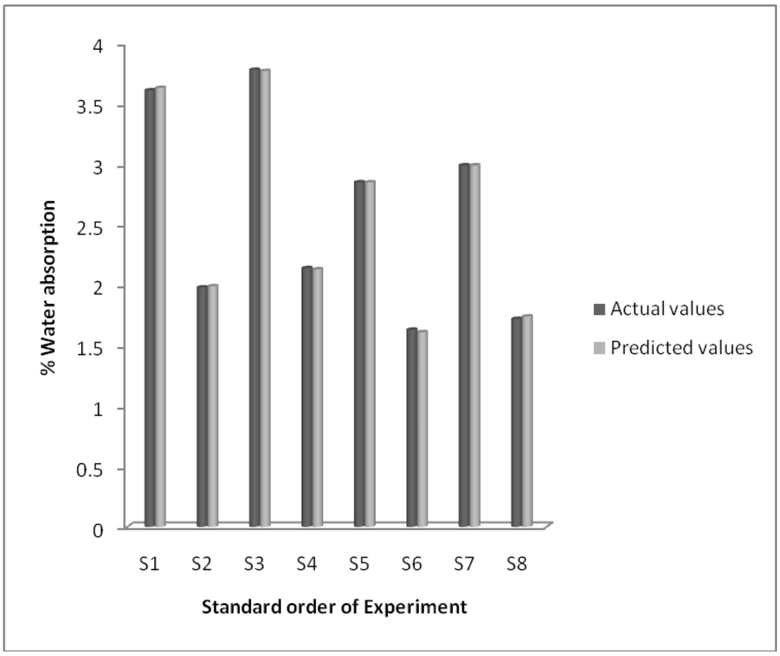


Figure 4.76: Variation of the % water absorption with experimental numbers for the RPFAp cement composites (Polyester)

Table 4.12: ANOVA for selected factorial model of the water absorption(RPFAp composites)

		%Water absorption for RPFAp composites (PVA)				
Source	Sum of Squares	DF	Mean square	F_{value}	P_{value}	Remarks
Model	3.525	2	1.76	352.91	<0.0001	Significant
A	2.18	1	2.18	436	< 0.0001	Significant
B	0.029	1	0.029	5.8	0.0461	Significant
C	1.345	1	1.345	269	< 0.0001	Significant
AB	0.00054	1	0.00054	0.108	0.0671	Not Significant
AC	0.0041	1	0.0041	0.82	0.0590	Not Significant
BC	0.0002	1	0.0002	0.04	0.023	Significant
ABC	0.00125	1	0.00125	0.25	0.078	NotSignificant
Residual	0.0251	5	0.005			
CorTotal	3.65	7				
		%Water absorption for RPFAp composites (Polyester)				
Model	4.94	4	1.23	1948.13		Significant
A	4.15	1	4.15	6548.21		Significant
B	0.0325	1	0.0325	61.89		Significant
C	0.673	1	0.673	1062.32		Significant
AB	0.00045	1	0.00045	0.710		Not Significant
AC	0.0761	1	0.0761	120.08		Significant
BC	0.00125	1	0.00125	1.974		Not Significant
ABC	0.0002	1	0.0002	0.316		Not Significant
Residual	0.0019	3	0.000633			
CorTotal	4.99	7				

4.12.2 Statistical Design and Modeling of the Compressive Strength

The results of the experiment are shown in Tables 4.13-4.14 for the RPF and RPFAp cement mortar resepectively.

Table4.13: Expanded plan matrix for factorial design of the RPF cement mortar (compressive strength)

S/n	x_0	A	B	C	AB	AC	BC	ABC	Compresive	
									PVA	Polyester
1	1	-1	-1	-1	+1	+1	+1	-1	9.05	9.05
2	1	1	-1	-1	-1	-1	+1	+1	11.05	10.08
3	1	-1	1	-1	-1	1	-1	+1	7.8	7.8
4	1	+1	+1	-1	+1	-1	-1	-1	9.29	8.0
5	1	-1	-1	+1	+1	-1	-1	+1	18.7	18.7
6	1	+1	-1	+1	-1	+1	-1	-1	20.1	19.8
7	1	-1	+1	+1	-1	-1	+1	-1	12.01	12.01
8	1	1	1	1	1	1	1	1	15.6	14.56
Effects(PVA)	12.95	2.12	-3.55	5.043	0.42	0.375	-0.25	0.68		
Effects(Polyester)	12.5	1.22	-3.815	7.535	0.155	0.605	-7.15	0.57		

Table4.14: Expanded plan matrix for factorial design of the RPFAp cement mortar (compressive strength)

S/n	x_0	A	B	C	AB	AC	BC	ABC	Compresive	
									PVA	Polyester
1	1	-1	-1	-1	+1	+1	+1	-1	10.5	10.5
2	1	1	-1	-1	-1	-1	+1	+1	11.2	10.5
3	1	-1	1	-1	-1	1	-1	+1	19.56	19.56
4	1	+1	+1	-1	+1	-1	-1	-1	20.9	20.21
5	1	-1	-1	+1	+1	-1	-1	+1	24.95	24.9
6	1	+1	-1	+1	-1	+1	-1	-1	25.66	25.6
7	1	-1	+1	+1	-1	-1	+1	-1	30.97	30.9
8	1	1	1	1	1	1	1	1	34.89	34.5
Effects(PVA)	22.43	1.932	8.60	13.28	1.23	0.412	-1.18	0.41		
Effects(Polyester)	22.08	1.238	8.42	13.78	0.088	2.24	0.97	0.56		

From the result of factorial design in Tables 4.13-4.14, the curing days appear to be the most important variable with main effect of (5.043, 7.535) and (13.28, 13.78) for the RPF and RPFAp composites respectively. These mean increasing the curing days from 1 to 28 days to raise the compressive strength. It can also be seen that the polymer-modified cement mortar has a positive effect on the compressive strength (2.12, 1.22) and (1.932, 1.238) for the RPF and RPFAp composites respectively. Also it was using the RPF that decreased the compressive strength by (-3.55, -3.815) for the PVA and polyester modified respectively. This means that increasing the volume percent of RPF from 0 to 25V% decreased the compressive strength. But a positive effect was observed for the RPFAp. The use of RPFAp increased the compressive strength by (8.60, 8.42) for the PVA and polyester modified respectively; this means that increasing the volume percent of RPF from 0 to 25V% increased the compressive strength. A positive effect were observed for all the interaction such as (AB, AC, BC and ABC) for the RPFAp cement mortar but when compared with the RPF cement mortar, only BC has negative effect (see Figures 4.77-4.84). Figures 4.78-4.84 showed the estimated response surface for compressive strength as a function of sample condition, volume percent and curing time. It can be seen that both forms of compressive strength were highly influenced by the sample condition (A) and curing time (C) and type of reinforcement (RPF and RPFAp). For the sample condition and curing time were found to increase when changing sample condition from unmodified to modified and curing time from 1 to 28 days. Also as volume percent of RPF (B) rise from 0.0 to 25V% compressive strength increases for only RPFAp composites(see Figures 4.78-4.84).

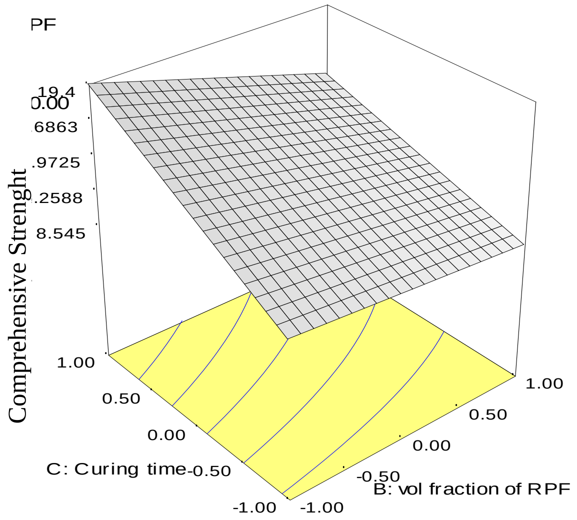


Figure 4.77: 3D surface plot of the effect of compressive strength for RPF mortar (PVA)

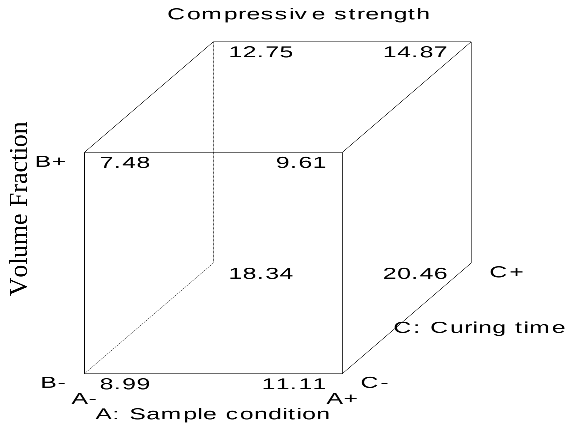


Figure 4.78: Cube plot of the effect of compressive strength for RPF mortar(PVA)

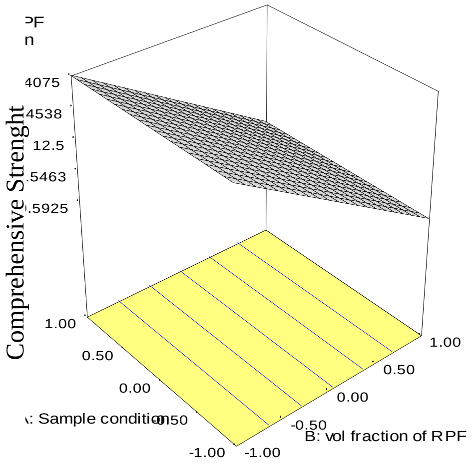


Figure 4.79: 3D surface plot of the effect of Compressive strength for RPF mortar (Polyester)

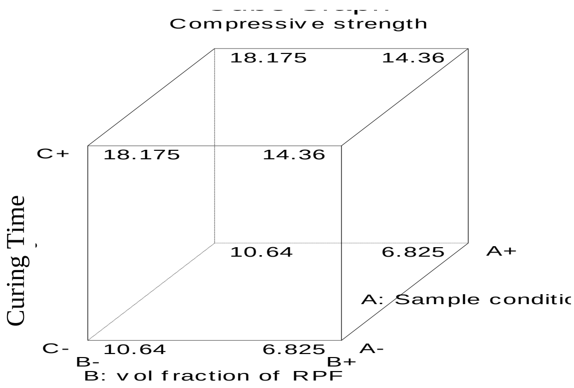


Figure 4.80: Cube plot of the effect of compressive strength for RPF mortar (Polyester)

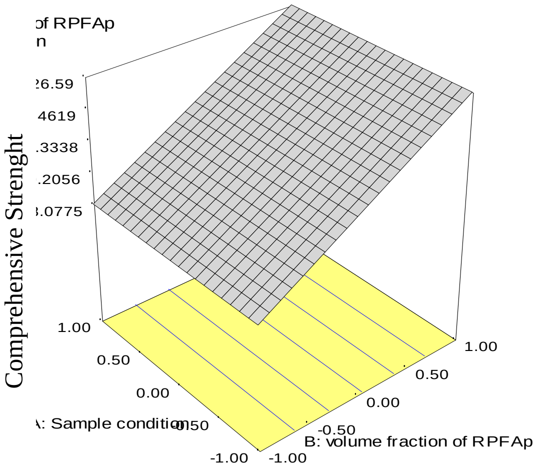


Figure 4.81: 3D surface plot of the effect of compressive strength for RPFAp mortar (PVA)

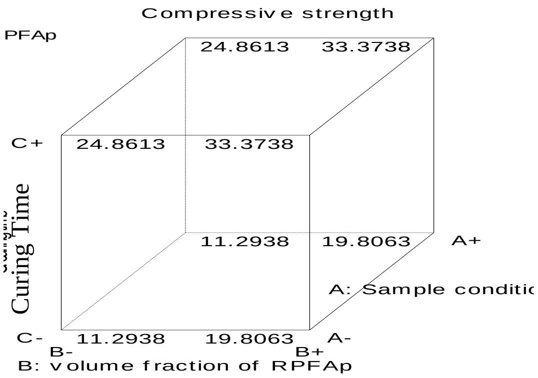


Figure 4.82: Cube plot of the effect of compressive strength for RPFAp mortar(PVA)

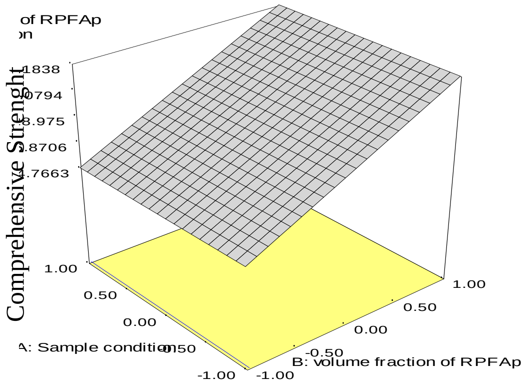


Figure 4.83: 3D surface plot of the effect of compressive strength for RPFAp mortar (Polyester)

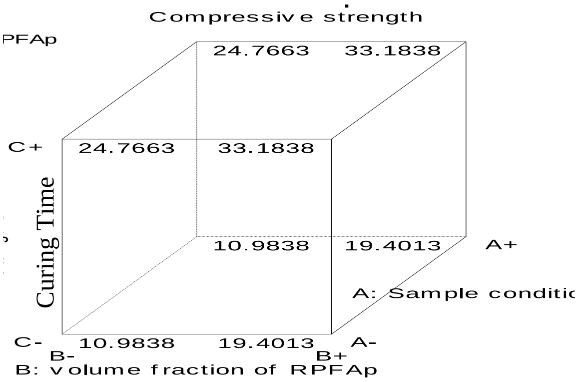


Figure 4.84: Cube plot of the effect of compressive strength for RPFAp mortar (Polyester)

Table 4.15 shown the ANOVA of the model of the compressive strength of the RPF composites(PVA). For the ANOVA of RPF cement composites (PVA) it was observed that the Model F-value of 72.45 implies that the model is significant. Also, values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case, A (sample), B (volume percent of RPF), C (curing time), BC (interaction between volume percent of RPF and curing time) are significant model terms. The "Pred R-Squared" of 0.9271 is in reasonable agreement with the "Adj R-Squared" of 0.9761. with a standard devation of 0.72 and mean of 12.95. The developed model equation for the compressive strength of RPF cement composites (PVA) was expressed as:

$$CS_{PVA} = 12.95 + 1.06A - 1.78B + 3.65C - 1.02BC \qquad (4.5)$$

Substituting the coded values of the variables for any experimental condition in Equation 4.5, the compressive strength for the RPF cement composites (PVA) can be calculated Figure 4.85 can be obtained.

Table 4.15: ANOVA for selected factorial model of the compressive strength (RPF composites)

		Compressive strength for RPF composites (PVA)				
Source	Sum of Squares	DF	Mean square	F_{value}	P_{value}	Remarks
Model	93.41	4	23.35	45.34	0.0026	Significant
A	8.989	1	8.989	17.45	*0.0250*	Significant
B	25.205	1	25.205	48.93	*0.0060*	Significant
C	50.85	1	50.85	98.73	*0.0007*	Significant
AB	0.3528	1	0.3528	0.6849	0.0567	Not Significant
AC	0.2813	1	0.2813	0.546	0.0678	Not Significant
BC	8.364	1	8.364	16.24	*0.0275*	Significant
ABC	0.9113	1	0.9113	1.769	0.0512	Not Significant
Residual	1.5454	3	0.5151			
CorTotal	94.954	7				
		Compressive strength for RPF composites (Polyester)				
Model	142.66	2	71.33	80.15	0.0023	Significant
A	2.98	1	2.98	3.35	0.0512	Not Significant
B	29.11	1	29.11	32.71	*0.0223*	Significant
C	113.55	1	113.55	127.56	*0.0013*	Significant
AB	0.0481	1	0.0481	0.054	0.0382	Significant
AC	0.732	1	0.732	0.822	0.0589	Not Significant
BC	0.05	1	0.05	0.056	0.0671	Not Significant
ABC	0.65	1	0.065	0.70	0.0614	Not Significant
Residual	4.46	5	0.89			
CorTotal	147.12	7				

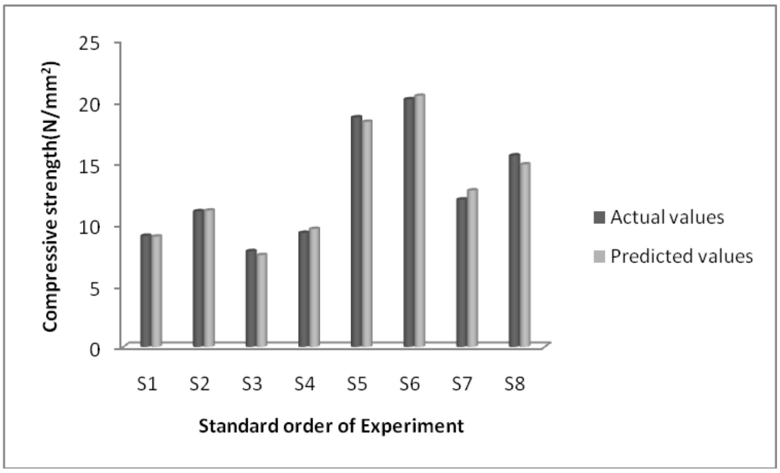


Figure 4.85: Variation of the compressive strength with experimental numbers for the RPF cement composites (PVA)

For the ANOVA of compressive strength of RPF cement composites (Polyester), it was observed that the Model F-value of 80.15 implies that the model is significant (see Table 4.15). Also values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case, B (volume percent of RPF),C (curing time) and the interaction AB are significant model terms. The "Pred R-Squared" of 0.7764 is in reasonable agreement with the "Adj R-Squared" of 0.8777 with a standard devation of 1.65 and mean of 12.5. The developed model equation for the compressive strength of RPF cement composites (Polyester) was expressed as:

$$CS_{PE} = 12.50 - 1.91B + 3.77C - 2.032AB \qquad (4.6)$$

Substituting the coded values of the variables for any experimental condition in Equation 4.5, the compressive strength for the RPF cement composites (polyester) can be calculated and shown in Figure 4.86.

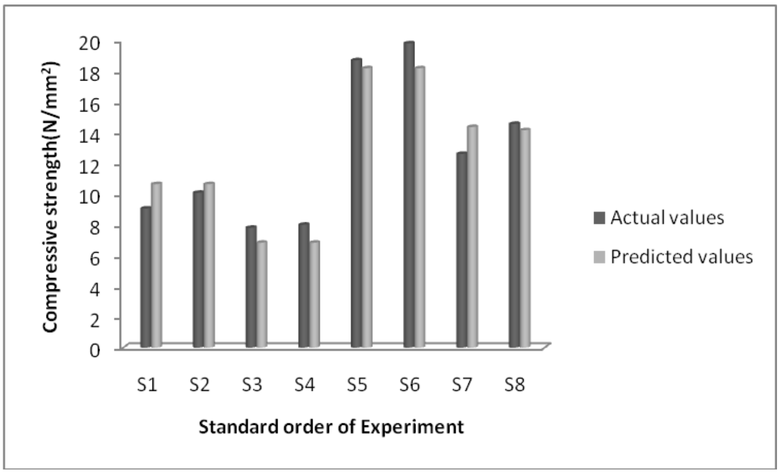


Figure 4.86: Variation of the compressive strength with experimental numbers for the RPF cement composites(Polyester)

Table 4.16 showed the ANOVA of the strength of RPFAp cement composites and the ANOVA of compressive strength of RPFAp cement composites (PVA). The Model F-value of 91.45 implies that the model is significant (see Table 4.16). Also values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case, A (sample condition), B (volume percent of RPF) and C (curing time) are significant model terms. The "Pred R-Squared" of 0.9477 is in reasonable agreement with the "Adj R-Squared" of 0.9714 with a standard devation of 1.46 and mean of 22.33. The model equation for the compressive strength of RPFAp cement composites (PVA) was expressed as:

$$CS_{Ap(PVA)} = 22.33 + 18.32A + 4.26B + 6.78C \qquad (4.7)$$

By substituting the coded values (+1, -1) of the variables for any experimental condition in Equation 4.7, the compressive strength for the RPFAp cement composites (PVA) can be calculated as shown in Figure 4.87.

Table 4.16: ANOVA for selected factorial model of the compressive strength (RPFAp composites)

		Compressive strength for RPFAp composites(PVA)				
Source	Sum of Squares	DF	Mean square	F_{value}	P_{value}	Remarks
Model	500.65	2	250.31	91.45	0.0001	Significant
A	7.47	1	7.47	2.73	0.0012	Significant
B	147.8	1	147.8	54.00	0.0004	Significant
C	352.85	1	352.85	128.92	0.0001	Significant
AB	3.038	1	3.038	1.11	0.0643	Not Significant
AC	0.340	1	0.340	0.12	0.079	Not Significant
BC	2.498	1	2.498	0.9113	0.0678	Not Significant
ABC	0.34	1	0.34	0.214	0.078	Not Significant
Residual	13.69	5	2.737			
CorTotal	514.34	7				
		Compressive strength for RPFAp composites (Polyester)				
Model	521.6	2	260.8	83.64	< 0.0001	Significant
A	3.06	1	3.06	0.981	0.0471	Significant
B	141.7	1	141.7	45.45	0.0003	Significant
C	379.9	1	379.9	121.84	0.0001	Significant
AB	0.0157	1	0.0157	0.005	0.124	Not Significant
AC	10.01	1	10.01	3.21	0.0434	Significant
BC	1.872	1	1.872	0.600	0.0712	Not Significant
ABC	0.633	1	0.633	0.321	0.0789	Not Significant
Residual	15.59	5	3.118			
CorTotal	537.19	7				

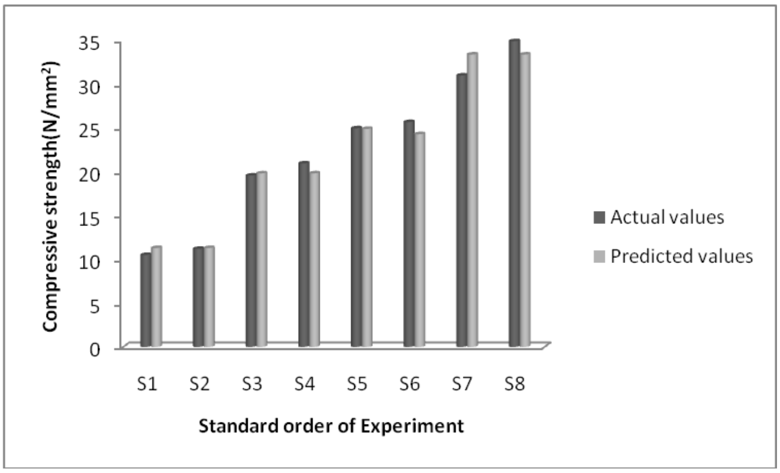


Figure 4.87: Variation of the compressive strength with experimental numbers for the RPFAp cement composites (PVA)

The ANOVA of compressive strength of RPFAp cement composites (Polyester). The Model F-value of 83.65 implies that the model is significant (see Table 4.16). Also values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case, A (sample condition), B (volume percent of RPF), C (curing time) and the interaction AC are significant model terms. The "Pred R-Squared" of 0.9575 is in reasonable agreement with the "Adj R-Squared" of 0.9768 with a standard devation of 1.33 and mean of 22.08. The model equation for the compressive strength of RPFAp cement composites (polyester) was expressed as:

$$CS_{Ap(PE)} = 22.08 + 1.09A + 4.21B + 6.89C - 0.675AC \qquad (4.8)$$

By substituting the coded values (+1, -1) of the variables for any experimental condition in Equation 4.7, the compressive strength for the RPFAp cement composites (polyester) can be calculated and shown in Figure 4.88.

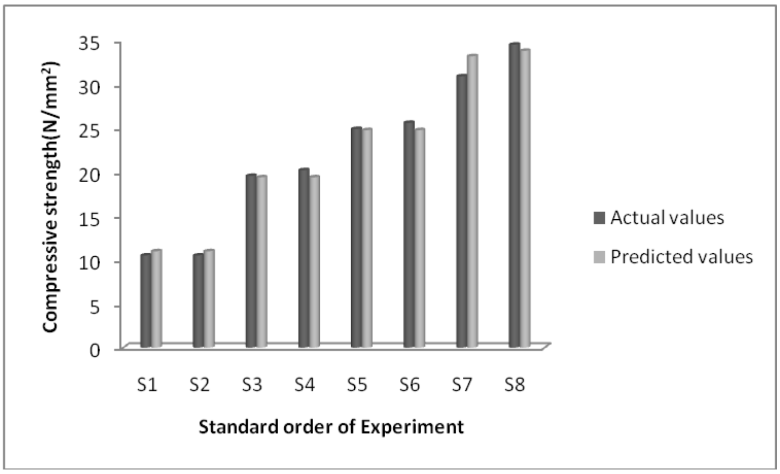


Figure 4.88: Variation of the compressive strength with experimental numbers for the RPFAp cement composites (Polyester)

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions are made.

1. The physico-mechanical properties of the raffia palm fibre compare favourably with those of some organic fibres used today for composite reinforcement as shown in table 2.4.
2. This study shows that pretreatment of raffia palm fibre with 0.25M NaOH Solution for 1hr followed by treatment with 80% ethanol in water with saline for two to three hours gives the best result of 136.329N/mm^{2}a and water absorption not more that three percent.
3. Factorial design of the experiment can be successfully employed to describe the silane treatment condition and the developed linear equation model can be used in predicting the tensile strength of the fibres within the selected experimental conditions.
4. Raffia palm (fibre and ash particles), PVA and polyester-modified cement mortar composite were successfully produced by casting method.
5. The density of the composites decreased as the volume percent of raffia palm fibre increased in the formulation. This means that light weight roofing sheets and other construction materials can be made with this formulation.
6. The water absorption decreased with increasing number of days of curing.
7. Analysis of tensile, compressive, flexural and impact strength showed that addition of the fibres improved the load bearing capacity of the composites.
8. Polymer modified samples have the best properties than unmodified samples.
9. The low values of water absorption recorded in this work for the polyester-modified cement mortar after curing for 28 days are within the recommend standard of 0 to 2% for roofing sheet application.

10. Thermal analysis result was clear that the RPFAp composites still retained above 80% of its weight at temperature around 900°C, while that of RPF composites still retained above 9% of its weight at temperature around 900°C.
11. Factorial design of the experiment can be successfully employed to describe the water absorption and compressive strength of the cement mortar, and the developed linear equation model can be used in predicting the water absorption and compressive strength of the composites within the selected experimental conditions.

5.2 Recommendations

The current study has yielded some important information about the microstructure and ageing behavior of polymer-modified cement mortar and its raffia palm fibre composites. In the course of the investigation, some recommendations and new areas of research have been identified.

1) It is recommended that the matrix-particle interface be investigated using high-resolution scanning electron microscopy (HRSEM) or high-resolution transmission electron microscopy (HRTEM).
2) Differential scanning calorimetry (DSC) experiment should be studied on this material.
3) The effect of chemical attacks should be investigated on the developed material
4) The blending of both RPF and RPFAp to produce a hybrid composites is recommended
5) The polymer-modified Raffia palm fibre composites should be used for roofing sheets, and that the volume fraction of the (RPF and RPFAp) should not exceed 20%vf

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6) Finally, the Federal Government of Nigeria and Raw Materials and Development Council are called upon to support further development of this novel material into commercial status.

5.3 Contributions to Knowledge

This research makes the following contributions to the body of knowledge in this field.

1. Data on chemical, thermal, mechanical and physical properties of Raffia palm fibre cement mortar composite have been experimentally determined.
2. Experimental modeling of the processing parameters of the cement mortar have been established

Publications

1. Experimental Evaluation of Rafia Palm Fiber Ash Particles Modified Polymer Cement Mortar Composites; Journal of the Chinese Advance Material Society (Taylor and Francis).
2. Characterization of the Thermomicrostrustural Analysis of Rafia Palm Fibers Proposed for Roofing Sheets Production; Journal of Mineral and Material Characterization and Engineering

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Comment [Kingsley29]: Why use 'et al' here when you been giving all the names of the authors?

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Appendix

Comment [Kingsley31]: Though more than one appendices, this segment is still called 'Appendix''

Appendix A

Table A1: Tensile properties of the pre-treatment

The tensile modulus(N/mm^2)						
	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25MNaOH	24167.0	2065.1	1952	929.6	1127.88	1360.23
0.50MNaOH	2286.1	1869.8	1123	1697.2	1757.12	1394.1
0.75MNaOH	1827.5	1340.9	1238.7	1538	1646.4	1497.93
1.00MNaOH	1251.4	1236.32	1530.3	1669	1409.14	1624.69
1.50MNaOH	1587.94	2247.3	1882	986.5	1762	2099.31
2.00MNaOH	1516.6	2109.7	958.2	1279	1303.58	1095.91
	The tensile strength(N/mm^2)					
	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25MNaOH	34.766	89.844	72.266	31.641	15.625	22.26
0.50MNaOH	24.766	58.594	32.031	39.453	43.59	15.625
0.75MNaOH	54.298	34.375	26.953	23.44	38.69	27.344
1.00MNaOH	35.156	38.673	31.25	26.953	38.672	47.266
1.50MNaOH	54.298	27.344	46.484	31.25	39.063	42.969
2.00MNaOH	38.673	27.344	26.953	15.625	15.625	58.984
	%Elongation					
	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25MNaOH	1.775	4	3.23	2.75	3	2.13
0.50MNaOH	2	3.375	4.5	2.48	2.75	2.5
0.75MNaOH	3.225	4.65	4.23	2.13	2.53	3.5
1.00MNaOH	3.5	3.25	2.25	1.75	4	4.25
1.50MNaOH	3.48	2.29	2.275	3.48	3.5	2.38
2.00MNaOH	3.2	0.98	2.43	4.75	3.25	4.38

Table A2: Tensile properties of the acetylation treatment

The tensile modulus(N/mm^2)						
Acetylation	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25M	1201.13	700.17	1432.29	914.72	1312.52	976.54
0.50M	920.14	1002.61	833.35	789.61	1064.16	1030.51
0.75M	596.77	423.54	1116.08	924.83	1906.39	1611.7
1.00M	329.99	572.92	419.81	492.38	1569.45	589.96
1.50M	398.44	387.9	703.13	511.69	462.97	1651.49
2.00M	1171.88	465.63	781.26	3920.51	963.99	896.7
	The tensile strength(N/mm^2)					
Acetylation	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25M	25.3906	12.50	11.7188	5.8594	3.5156	11.7188
0.50M	15.625	15.2344	7.8125	9.8125	3.90625	4.2969
0.75M	15.625	11.7188	11.7188	3.9063	7.8125	7.8125
1.00M	19.5313	18.625	11.7188	12.1094	11.7188	20.3125
1.50M	17.8781	15.2344	11.7188	17.5781	7.8125	15.625
2.00M	9.7656	11.7188	12.500	7.8125	15.625	16.0125
	%Elongation					
Acetylation	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25M	3.25	2.38	2.5	2.5	2.25	1.23
0.50M	2.5	1.5	1.88	2	1.5	1.75
0.75M	2.75	1.75	1.75	2.5	2.2	1.8
1.00M	2.23	1.25	1.23	2.38	2.25	2
1.50M	1.5	1.5	1.25	2.38	2.25	2.25
2.00M	1.5	1.38	1	2.38	2.75	2

Table A3: Tensile properties of the $KMNO_4$ treatment

The tensile modulus(N/mm^2)						
%$KMNO_4$	0.5min	1min	1.5min	2min	2.5min	3min
0.25%$KMNO_4$	1494.67	1160.57	762.47	844.8	994.07	1840.33
0.5%$KMNO_4$	924.41	669.64	577.58	717.3	1315.21	843.45
0.75%$KMNO_4$	657.86	1447.14	878.12	857.96	1280.39	1155.57
1%$KMNO_4$	1040.84	947.8	1022.68	1302.08	1614.71	1104.91
1.25%$KMNO_4$	1263.34	933.94	1000.43	1019.4	1272.11	716.15
1.5%$KMNO_4$	1263.34	757.89	2017.15	937.5	833.34	909.901
	The tensile strength(N/mm^2)					
%$KMNO_4$	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25	26.56	31.88	11.88	12.81	34.38	31.8
0.5	29.69	12.5	9.96	28.13	21.56	25
0.75	10.94	22.81	18.75	12.5	15.31	15.63
1	14.06	12.81	12.5	12.5	15.63	9.06
1.25	18.875	25	9	13.13	9.38	9.38
1.5	9.38	21.88	10.5	6.25	6.25	6.25
	%Elongation					
%$KMNO_4$	30min	1hour	1.5hour	2hours	2.5hours	3hours
0.25	4.5	3	2.25	2.25	5.13	2.5
0.5	5.25	3.5	4.38	4	2.62	3
0.75	3	3	3.25	3.375	2.25	1.3
1	2.25	2.5	2.48	2	1.75	1.75
1.25	2.25	3.25	2.13	2	1.13	2
1.5	3	3.13	3	1.25	2	1.38

Table A4: Tensile properties of the SLS treatment

	The tensile modulus(N/mm^2)					
%SLS	30min	1hour	1.5hour	2hours	2.5hours	3hours
5	2460.94	1531.15	1223.97	723.39	1297.74	818.33
10	601.92	1206.46	727.78	841.75	599.9	834.48
15	1200.08	1076.41	968.81	1096.12	914.35	1064.66
20	1156.13	1069.23	833.03	1140.4	1672.35	803.29
25	1829.05	3165.07	1285.31	1352.83	1036.74	670.88
30	534.79	700.29	674.76	1245.79	509.09	1468.57
	The tensile strength(N/mm^2)					
%SLS	30min	1hour	1.5hour	2hours	2.5hours	3hours
5%SLS	28.13	57.81	31.88	12.5	43.75	31.25
10%SLS	10.94	17.19	16.25	12.5	10.94	15.63
15%SLS	38.94	21.88	15.63	15.31	9.06	27.5
20%SLS	9.38	21.88	40.63	15	18.75	15.63
25%SLS	28.94	21.88	9.38	21.56	15.63	11.88
30%SLS	15.63	18.63	23.75	16.25	15.66	18.125
	%Elongation					
%SLS	30min	1hour	1.5hour	2hours	2.5hours	3hours
5	1.5	3.75	3.5	4.25	3.75	5.75
10	2.75	3.28	5	2.48	4.75	2.75
15	3.75	3.75	2	2.75	2.25	4.25
20	1.75	3.63	5.75	3.25	1.38	3.25
25	2.225	1.63	2.8	3.25	3.25	3
30	3	2.75	4	2.48	7	2.75

Table A5: Tensile properties of the silane treatment

The tensile modulus(N/mm^2)						
Ethanol/water	30min	1hour	1.5hour	2hours	2.5hours	3hours
30/70	649.71	2254.46	2512.17	1395.68	1717.98	2715.08
40/60	998.57	1928.78	1933.10	2458.96	1269.17	836.78
50/50	505.31	1584.28	2738.60	2296.62	926.66	542.52
60/40	2883.87	2744.10	1978.85	1642.62	2661.68	669.21
70/30	1575.48	1939.05	1699.76	3260.09	2623.73	2136.20
80/20	2182.52	3526.52	1554.85	4488.62	1672.52	3141.62
	The tensile strength(N/mm^2)					
Ethanol/water	30min	1hour	1.5hour	2hours	2.5hours	3hours
30/70	19.53	102.34	42.34	72.27	39.45	112.11
40/60	29.30	35.16	64.45	93.75	32.42	15.643
50/50	29.30	54.69	62.50	89.84	19.53	11.72
60/40	66.78	78.91	31.25	35.16	70.313	56.64
70/30	58.59	59.39	62.89	64.45	54.69	81.64
80/20	86.32	93.36	85.93	136.33	100.78	121.30
	%Elongation					
Ethanol/water	30min	1hour	1.5hour	2hours	2.5hours	3hours
30/70	5.60	4.25	2.75	5.0	2.50	3.50
40/60	6.37	2.50	3.50	3.75	3.25	5.00
50/50	6.63	3.00	2.75	4.50	4.25	4.00
60/40	4.13	3.75	2.48	3.25	2.50	9.75
70/30	3.63	4.38	3.98	2.00	2.50	4.75
80/20	5.25	3.5	4.25	4.38	6.25	2.30

Table A6: Caption of the FLTR band of RPFAp

No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	432.05	0.759	0.5221	455.2	401.19	22.8471	13.2525
2	501.49	0.8948	0.3658	532.35	462.92	49.1049	14.4998
3	594.08	1.489	0.5612	617.22	540.07	79.7366	16.537
4	678.94	1.9448	0.8191	732.95	624.94	157.9544	37.0474
5	763.81	1.5614	0.3696	786.96	740.67	65.2301	9.8464
6	825.53	1.6954	0.5523	864.11	794.67	99.6994	20.3267
7	902.69	1.7565	0.5453	964.41	871.82	135.9871	24.273
8	1010.7	2.1549	0.8217	1087.85	972.12	204.0077	44.5988
9	1134.14	1.9792	0.5375	1165	1095.57	121.5144	19.7567
10	1219.01	1.9341	0.2395	1234.44	1172.72	102.8476	8.2471
11	1319.31	1.9705	0.4576	1342.46	1280.73	111.0766	14.6337
12	1381.03	2.0568	0.4862	1396.46	1350.17	81.1079	12.2169
13	1427.32	1.8866	0.319	1489.05	1404.18	145.7087	14.0073
14	1535.34	1.6272	0.1659	1581.63	1496.76	132.5203	8.5047
15	1674.21	2.1804	0.7586	1728.22	1612.49	202.4505	37.3994
16	1759.08	1.5459	0.2515	1813.09	1735.93	102.7431	6.3779
17	1836.23	1.2148	0.0972	1890.24	1813.09	89.0801	3.956
18	1921.1	1.2603	0.0972	1890.24	1813.09	89.0801	3.956
19	1982.82	1.3263	0.1623	2021.4	1951.96	85.9229	5.0974
20	2113.98	1.2462	0.0443	2129.41	2090.84	46.8976	0.9381
21	2198.85	1.2253	0.0371	2222	2175.7	55.9817	0.8879
22	2268.29	1.2888	0.0987	2299.15	2229.71	85.6853	3.2093
23	2360.87	1.5328	0.3548	2399.45	2306.86	125.0002	15.4824
24	2507.46	1.3836	0.1109	2546.04	2484.32	82.1754	3.4944
25	2592.33	1.3823	0.122	2615.47	2553.75	82.5614	4.1612
26	2654.05	1.6622	0.3023	2677.2	2623.19	80.0736	8.3102
27	2708.06	1.4675	0.0399	2723.49	2684.91	56.0725	0.9037
28	2754.35	1.5799	0.214	2777.5	2731.2	68.8328	5.1699
29	2808.36	1.8081	0.3959	2831.5	2785.21	75.2159	10.0711
30	2862.36	1.7971	0.2784	2885.51	2839.22	77.0421	6.9826
31	2947.23	1.9323	0.3031	2978.09	2916.37	109.8406	9.3848
32	3047.53	2.1608	0.3343	3078.39	2985.81	177.5833	13.7889
33	3101.54	2.046	0.2283	3155.54	3086.11	127.5642	6.3491
34	3217.27	2.0002	0.4915	3248.13	3163.26	147.6798	18.8786
35	3271.27	1.7895	0.0873	3278.99	3255.84	37.9063	0.5288
36	3325.28	2.0778	0.4134	3348.42	3294.42	103.8436	12.0693
37	3379.29	1.6944	0.1894	3417.86	3356.14	100.3776	7.8169
38	3441.01	1.6254	0.2157	3456.44	3425.58	47.9399	3.8451
39	3495.01	1.841	0.3831	3518.16	3464.15	87.5406	11.4796
40	3579.88	1.5912	0.2269	3610.74	3564.45	68.7754	5.9944
41	3641.6	1.448	0.1756	3664.75	3618.46	63.1353	4.219
42	3687.9	1.4941	0.2375	3711.04	3672.47	53.653	5.177
43	3803.63	1.3715	0.193	3842.2	3757.33	108.8106	10.8637
44	3873.06	1.4348	0.2338	3888.49	3849.92	52.5421	5
45	3919.35	1.4983	0.4618	3942.5	3896.21	59.0629	10.8736

Table A7: Caption of the FLTR band of RPF

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr Area
1	624.94	1.1637	0.6473	671.23	540.07	101.335	41.9376
2	709.8	1.1757	0.3706	732.95	678.94	51.1586	10.007
3	771.53	1.2223	0.3796	802.39	740.67	65.3141	12.3309
4	840.96	1.4463	0.4641	864.11	810.1	63.4171	13.5888
5	902.69	1.4376	0.3338	925.83	871.82	70.608	10.1478
6	956.69	1.2703	0.1661	972.12	933.55	44.3485	3.4226
7.	1026.13	1.7435	0.5806	1072.42	979.84	137.0762	29.0254
8	1111	1.4904	0.2029	1134.14	1080.14	74.0094	6.4792
9	1157.29	1.5794	0.2375	1203.58	1141.86	88.9468	10.044
10	1234.44	1.959	0.661	1273.02	1211.3	102.8968	21.4774
11	1357.89	1.5171	0.1374	1373.32	1327.03	64.6068	3.7317
12	1319.61	1.7837	0.4115	1496.76	1381.03	176.9997	21.7816
13	1527.62	1.3915	0.1764	1558.48	1504.46	71.14	5.5171
14	1597.06	1.5797	0.3035	1627.92	1566.2	88.0422	9.9166
15	1658.78	1.4722	0.1485	1705.07	1635.64	96.761	6.04
16	1751.36	2.5047	1.1192	1789.94	1712.79	146.8746	41.4452
17	1820.8	2.0322	0.5493	1843.95	1797.66	84.1359	14.2621
18	1882.52	1.7499	0.3727	1921.1	1851.66	108.9844	13.3595
19	1967.39	2.0751	0.5596	1998.25	1928.82	123.1494	18.2756
20	2052.26	1.8061	0.2636	2067.69	2005.97	102.9765	7.4095
21	2098.55	1.738	0.2204	2129.41	2075.41	88.6114	6.6548
22	2160.27	1.8298	0.2624	2183.42	2137.13	79.3305	6.691
23	2214.28	2.1089	0.4804	2260.57	2191.13	128.4229	14.1926
24	2283.72	1.9223	0.3806	2314.58	2268.29	80.8147	11.6555
25	2407.16	1.7091	0.2696	2430.31	2322.29	155.851	15.2967
26	2461.17	1.7827	0.1427	2476.6	2438.02	64.4349	2.8667
27	2553.75	1.9018	0.3893	2576.9	2522.89	93.6651	11.2156
28	2623.19	1.9053	0.4708	2684..91	2584.61	170.1726	26.9596
29	2792.93	1.755	0.2169	2808.36	2769.78	64.2701	4.8307
30	2839.22	1.9849	0.4737	2862.36	2816.07	82.0509	11.9484
31	2900.94	1.7251	0.0762	2908.65	2870.08	62.5566	2.5109
32	3047.53	2.0129	0.4878	3086.11	2993.52	163.3778	22.7255
33	3116.97	2.1043	0.6009	3186.4	3093.82	158.7182	25.8657
34	3217.27	1.4155	0.0977	3232.7	3194.12	52.8833	2.408
35	3286.7	1.7686	0.2418	3309.85	3240.41	111.4324	9.5466
36	3487.3	1.4798	0.1136	3502.73	3433.29	94.8338	4.78
37	3541.31	1.6388	0.1725	3556.74	3510.45	70.4679	3.8229
38	3610.74	1.7231	0.4506	3664.75	3595.31	99.0638	17.6244
39	3703.33	1.4873	0.4561	3734.19	3672.47	79.6477	17.0259
40	3765.05	1.2936	0.1546	3803.63	3741.9	77.1671	6.9878
41	3834.49	1.4362	0.4558	3857.63	3811.34	57.1563	11.0811
42	3903.92	1.4493	0.5669	3942.5	3865.35	89.2287	21.415

Table A8: Results of the density for the various formulations

	Density of RPFAp(g/cm^3) after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	2.299	2.281	2.278	2.271	2.261	2.244
Polyester modified	2.223	2.204	2.197	2.190	2.182	2.162
PVA modified	2.193	2.188	2.171	2.162	2.150	2.139
	Density of RPF(g/cm^3) after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	2.209	2.198	2.195	2.189	2.177	2.168
Polyester modified	2.121	2.113	2.111	2.103	2.092	2.082
PVA modified	2.077	2.068	2.058	2.055	2.049	2.040

Table A9: Results of the % of Water absorption for the various formulations for RPF

Volume %	% of Water Absorption Of The RPF For Unmodified Cement Mortar					
	1day	3days	7days	14days	21days	28days
0	4.130	4.100	3.960	3.930	3.560	3.340
5	4.134	4.130	4.010	3.990	3.780	3.550
10	4.140	4.134	4.130	4.050	3.850	3.780
15	4.200	4.160	4.140	4.130	4.120	4.110
20	4.310	4.230	4.210	4.200	4.178	4.170
25	4.520	4.450	4.350	4.320	4.300	4.280
	% of Water Absorption of the RPF for Polyester modified cement mortar					
0	2.85	2.81	2.55	2.35	2.22	2.21
5	2.85	2.83	2.56	2.43	2.24	2.21
10	2.91	2.83	2.58	2.46	2.35	2.31
15	2.95	2.85	2.58	2.55	2.44	2.35
20	3	3.13	2.67	2.57	2.44	2.36
25	3.01	3.2	2.68	2.47	2.45	2.45

	% of Water Absorption of the RPF for PVA modified cement mortar					
0	3.01	2.99	2.65	2.55	2.45	2.34
5	3.06	3.01	3	2.67	2.55	2.38
10	3.12	3.111	3.06	2.81	2.58	2.52
15	3.15	3.11	3.07	2.85	2.65	2.55
20	3.21	3.13	3.1	2.88	2.77	2.59
25	3.29	3.2	3.16	2.98	2.9	2.61

Table A10: Results of the % of Water absorption for the various formulations for RPFAp

Volume %	% of Water Absorption Of The RPFAp For Unmodified Cement Mortar					
	1day	3days	7days	14days	21days	28days
0	3.61	3.42	3.21	3.11	2.99	2.85
5	3.62	3.45	3.25	3.13	2.99	2.87
10	3.64	3.46	3.27	3.144	3	2.89
15	3.65	3.5	3.3	3.15	3.02	2.9
20	3.77	3.55	3.45	3.21	3.04	2.94
25	3.78	3.57	3.48	3.28	3.1	2.99
	% of Water Absorption Of The RPFAp For polyester modified Cement Mortar					
0	1.98	1.92	1.89	1.85	1.8	1.63
5	2.05	1.92	1.9	1.85	1.8	1.62
10	2.1	1.93	1.95	1.89	1.81	1.67
15	2.1	1.93	1.99	1.9	1.9	1.67
20	2.12	1.96	1.99	1.92	1.9	1.7
25	2.14	1.97	2	1.93	1.91	1.72
	% of Water Absorption Of the RPFAp For PVA modified cement mortar					
0	2.67	2.01	1.89	1.85	1.8	1.77
5	2.67	2.05	1.91	1.86	1.8	1.75
10	2.68	2.1	1.95	1.89	1.85	1.77
15	2.69	2.13	1.99	1.92	1.9	1.84
20	2.7	2.13	1.99	1.92	1.9	1.86
2.5	2.72	2.15	2	1.93	1.91	1.89

Table A11: Results of the % of Water absorption for the various formulations for RPFAp

Volume percent	% of Water Absorption of the RPFAp For unmodified cement mortar					
	1day	3days	7days	14days	21days	28days
0	70.1	72.0	72.9	74.9	76.5	78.9
0.5	68.9	70.0	70.1	74.1	76.0	77.9
1	62.5	64.4	64.5	71.5	75.4	77.5
1.5	60.4	62.8	64.0	68.9	75.0	77.5
2	58.8	59.0	60.7	63.4	70.0	75.8
2.5	56.0	56.4	58.9	62.0	70.0	75.0
	% of Water absorption of the RPFAp For polyester modified cement mortar					
0	95.6	95.9	94.0	92.1	90.0	90.0
0.5	93.4	93.4	90.8	89.5	88.5	85.6
1	88.9	86.5	84.9	82.8	82.0	80.1
1.5	86.0	86.0	81.0	80.1	79.0	78.9
2	84.0	82.0	80.8	79.4	79.0	77.9
2.5	83.0	80.3	80.0	78.9	76.4	86.0
	% of Water absorption of the RPFAp for PVA modified cement mortar					
0	2.67	2.01	1.89	1.85	1.8	1.77
0.5	2.67	2.05	1.91	1.86	1.8	1.75
1	2.68	2.1	1.95	1.89	1.85	1.77
1.5	2.69	2.13	1.99	1.92	1.9	1.84
2	2.7	2.13	1.99	1.92	1.9	1.86
2.5	2.72	2.15	2	1.93	1.91	1.89

Table A12: Results of the compressive strength for the various formulations for RPFp

Volume %	Compressive Strength(N/mm^2) of the RPFAp for unmodified cement mortar					
	1day	3days	7days	14days	21days	28days
0	10.5	11.4	15.6	20.5	22.6	24.9
5	12.6	12.9	16.8	21.5	23.8	25.6
10	16.7	18.9	19.0	24.8	25.9	26.7
15	18.9	20.0	21.8	27.8	29.0	29.7
20	18.9	20.5	23.4	28	29.5	29.8
25	19.56	23	25.7	29.8	30.5	30.9
	Compressive Strength(N/mm^2) of The RPFAp for polyester modified cement mortar					
0	10.5	12.4	15.6	20.5	22.6	25.6
5	13.8	14.56	17.8	23.6	25.3	27.9
10	17.8	18.9	23.4	24.8	25.9	28.9
15	18.9	23.5	24.8	27.8	28.8	29.8
20	18.9	24	26.7	30.7	32.3	32.89
25	20.21	24.78	30.45	32.6	34.1	34.5
	Compressive Strength(N/mm^2) of The RPFAp for PVA modified cement mortar					
0	11.2	13.4	15.6	23.6	24.7	25.6
5	13.8	15.67	17.8	24.5	25.3	28.8
10	17.8	19.78	23.4	25.67	25.9	30.23
15	18.4	23.5	25.67	27.8	29.01	30.78
20	18.9	24.5	26.7	31.67	33.1	33.67
25	21.9	23.56	30.45	33.7	34.1	34.89

Table A13: Results of the Compressive strength for the various formulations for RPF

Volume %	Compressive Strength(N/mm^2) of The RPF for unmodified cement mortar					
	1day	3days	7days	14days	21days	28days
0	9.05	11.23	15.6	16.7	17.8	18.7
5	9.01	11	14.5	14.3	13.78	13.67
10	9	11	13.4	14.1	13.45	13.01
15	8.67	10.5	12.34	13.67	13.21	13
20	8.1	9.23	11.2	12	12.67	12.78
25	7.8	8.91	10.05	11.67	12.4	12.01
	Compressive Strength(N/mm^2) of The RPF for polyester modified cement mortar					
0	10.08	14.5	15.6	17	17.8	19.8
5	9.01	11	14.5	14.3	13.78	13.67
10	9	11	13.4	14.1	14.23	15.78
15	8.67	10.5	12.34	13.67	13.21	15.46
20	8.1	9.23	11.2	12	12.67	12.78
25	8	9.01	11	11.67	12.89	14.56
	Compressive Strength(N/mm^2) of The RPF for PVA modified cement mortar					
0	11.05	14.5	15.6	17	17.8	20.1
5	10.6	14.1	14.5	15.4	16.78	18.7
10	10.1	14	14.3	15.6	16	18.23
15	9.67	10.5	12.34	13.67	16.78	17.89
20	9.34	9.23	12	13.23	15.1	16.7
25	9.29	9.01	11.67	12.78	14.5	15.6

Table A14: Results of the flexural strength for the various formulations

	Flexural strength(N/mm^2) of RPFAp composites after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	5.85	5.21	4.65	4.23	4.00	3.85
Polyester modified	5.98	5.68	5.56	5.24	4.98	4.89
PVA modified	5.98	5.98	4.72	4.67	4.50	4.23
	Flexural strength(N/mm^2) of RPF composites after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	6.70	8.7	10.8	10.9	12.3	12.7
Polyester modified	6.89	9.23	11.14	11.90	12.9	13.4
PVA modified	6.90	10.70	11.89	12.34	13.78	13.78

Table A15: Results of the Tensile strength for the various formulations

	Tensile strength(N/mm^2) of RPFAp composites after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	3.85	3.21	2.65	2.23	2.00	1.85
Polyester modified	3.98	3.68	3.56	3.24	2.98	2.57
PVA modified	3.98	3.98	3.72	3.67	3.50	3.00
	Tensile strength(N/mm^2) of RPF composites after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	3.85	4.10	4.30	4.52	4.89	4.99
Polyester modified	4.10	4.60	5.10	5.55	5.78	5.89
PVA modified	4.50	4.90	4.90	5.80	5.91	6.01

Table A16: Results of the impact energy for the various formulation

	Impact Energy(J) of RPFAp composites after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	2.85	2.21	1.65	1.23	1.00	0.95
Polyester modified	2.98	2.60	2.55	1.24	1.48	1.35
PVA modified	2.98	2.98	2.62	1.67	1.50	1.45
	Impact Energy(J) of RPF composites after 28days of curing					
	0V%	5V%	10V%	15V%	20V%	25V%
Unmodified	3.70	3.7	4.8	4.9	5.01	5.02
Polyester modified	3.89	4.01	5.01	5.90	5.91	6.01
PVA modified	3.90	4.70	5.21	5.98	6.23.	6.34

Appendix B:

Comment [Kingsley32]: Title of appendix

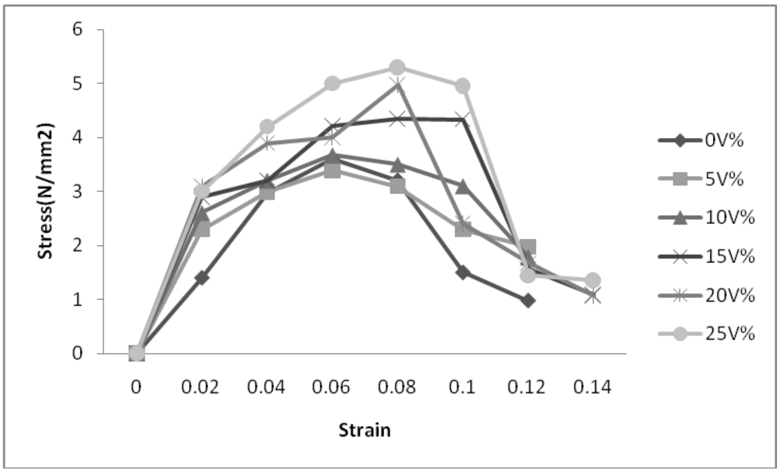

Figure B1: The Stress-Strain curve of the unmodified RPF Composites

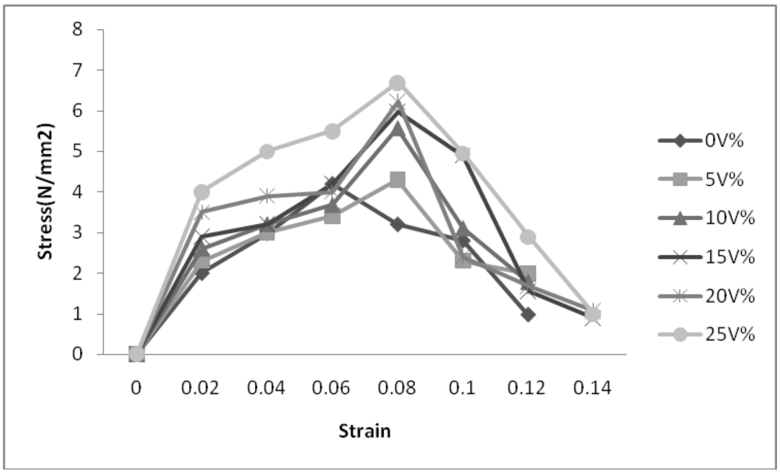

Figure B2: The Stress-Strain curve of the PVA modified RPF Composites

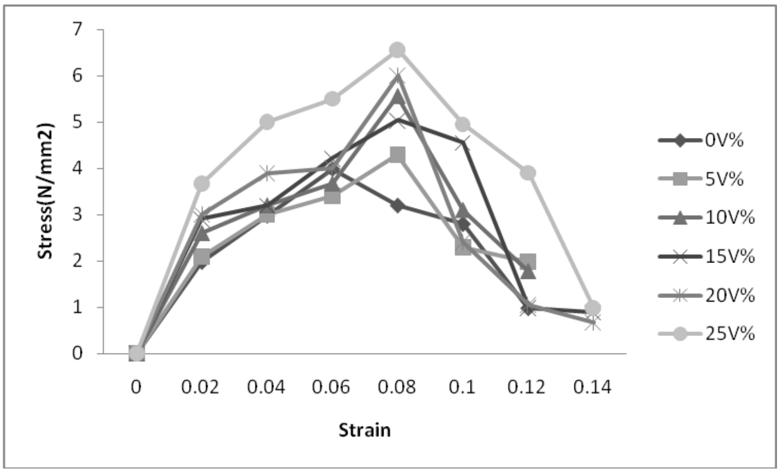

Figure B3: The Stress-Strain curve of the Polyester modified RPF Composites

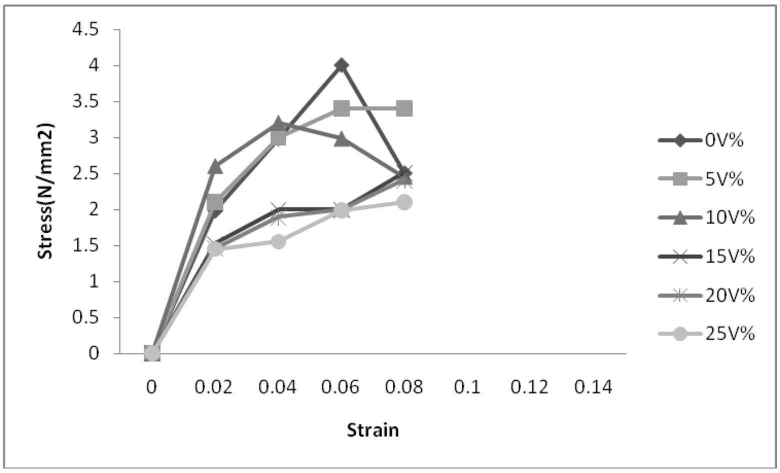

Figure B4: The Stress-Strain curve of the unmodified RPFAp Composites

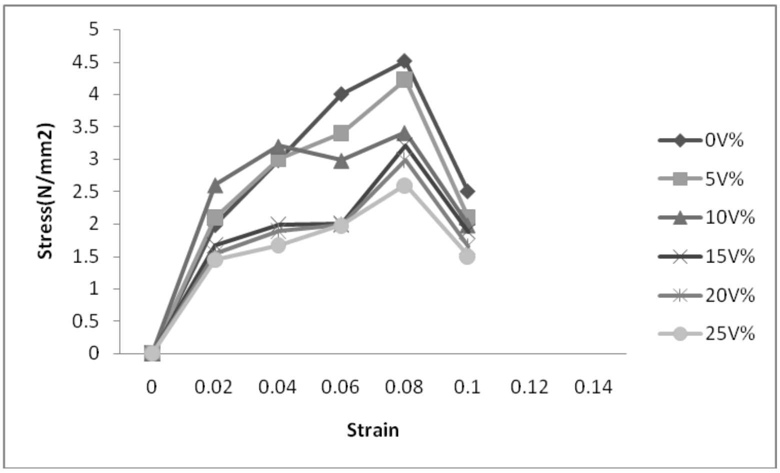

Figure B5: The stress-strain curve of the PVA modified RPFAp composites

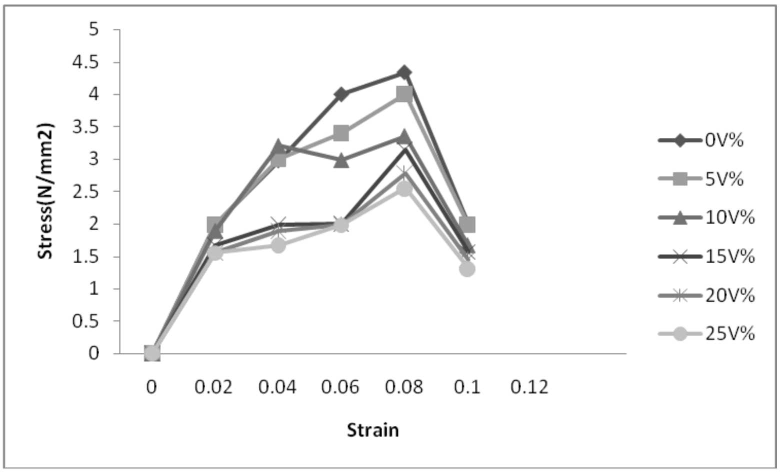

Figure B6: The stress-strain curve of the polyester modified RPFAp composites