



**JIMMA UNIVERSITY
JIMMA INSTITUTE OF TECHNOLOGY
SCHOOL OF MATERIAL SCIENCE AND ENGINEERING**

**IMPROVING HYDRATION TIME AND COMPRESSIVE STRENGTH OF
ETHYLENE-VINYL ACETATE POLYMER-MODIFIED CEMENT
USING EGGSHELL ASH**

A Thesis submitted to School of Graduate Studies, Jimma University, Jimma Institute of Technology, School of material science and engineering in Partial Fulfillment of the Requirements for the Degree Master of Science in Ceramic engineering

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DECLARATION

The thesis is my original work and has not been presented for a degree in any other university.

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ABSTRACT

Polymers added to cement to enhance its physical properties retards its hydration reaction and reduces its compressive strength. Eggshell ash added to polymer-modified cement to enhance its physical properties can accelerate its hydration reaction and increases its compressive strength. Also, this study presents a simple way of recycling Ethylene-vinyl acetate polymer and eggshell wastes as a constituent in a mix of lightweight mortar and to evaluate its efficiency to produce a mortar with high strength and lightweight. The mechanism of improving the physical properties of polymer modified cement composites using an eggshell was investigated by setting time, compressive strength test, and X-Ray diffractometer with various ratios of (15%, 30%, 45%, 60%) eggshell to polymer-modified cement. It is found that increasing the amount of eggshell caused an acceleration in hydration reaction and an increase in compressive strength. The initial and final setting time which is found in a polymer –cement composite was 261 and 403 minutes respectively, the incorporation of 60% eggshell ash with polymer-modified cement reduced the time to 222 and 356 minutes respectively. The 7th and 28th- day compressive strength of Polymer-cement composite was 3.39 MPa and 6.5Mpa respectively, this was improved to 4.84 MPa and 7.87 MPa respectively, and this is fulfilled by incorporation of 60% of eggshell ash with the Polymer- cement composite. From an XRD result, it is found that the intensities of Ca(OH)₂ peak at an angle $2\theta = 18^\circ$ and 47° increased with the increase in eggshell ash. The increase in yield of calcium ions reduces retardation in a hydration reaction.

Keywords: Polymer- modified cement, Ethylene-vinyl acetate, Eggshell ash, hydration of cement, compressive strength of cement, calcium ions

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ACRONYMS

EVA	Ethylene-vinyl acetate
ESA	Eggshell ash
OPC	Ordinary Portland cement
PPC	Portland pozzolana cement
ASTM	American society for testing and Materials

CHAPTER - ONE

INTRODUCTION

1.1 Background

Cement is the World's most important building material which is used in the construction industry. It is a widely used and consumed resource on the earth. Mainly used as a binding material for the production of many structures that make up the modern World including buildings, bridges, harbors, runways, and roads. Cement used in construction are usually inorganic often contains lime and calcium Silicate based compounds.

Portland cement is one of the widely used cement types in the world, for different construction purposes. High stiffness, high compressive strength, low cost, ease of fabrication, Fineness, Soundness and, etc. makes them the favorite cement in the world. Despite these advantages, it has a limitation: like low tensile and flexural strength, low strain capacity, brittleness, permeability, long term durability, which is needed to be improved. To reduce such problems polymers are added as a modifier. Polymers like acrylic, polyvinyl acetate, and ethylene-vinyl acetate are widely used to modify the physical properties of cement. As a result, the polymer-cement composite achieved better properties in tensile and flexure strength, elasticity, adhesiveness, water tightness, chemical resistance, waterproofing capacity, freeze-thaw resistance, but low compressive strength and delayed hydration reaction has resulted. This research paper deals with improving the compressive strength and hydration time of polymer modified cement mortar.

Mortar and concrete made with Portland cement have been a popular construction material in the world for the past 170 years or more. However, cement mortar and concrete have some disadvantages such as delayed hardening, low tensile strength, large drying shrinkage, and low chemical resistance. To reduce these disadvantages, many attempts to use polymers have been made. One

such attempt is polymer-modified (or polymer-cement) mortar or concrete, which is made by modifying ordinary cement mortar or concrete with polymer additives such as latexes, redispersible polymer powders, water-soluble polymers, liquid resins, and monomers [1].

In this paper, Ethylene-vinyl acetate (EVA) is used as cement modifier. Ethylene-vinyl acetate (EVA) is a copolymer of Ethylene and vinyl acetate. Ethylene is a group of alkenes, which contain carbon-carbon double bonds. It is a colorless, flammable gas having a sweet test and odor. Vinyl acetate is an organic compound that is a colorless liquid and is a precursor to polyvinyl acetate. EVA is produced by a high temperature/high-pressure processor or with an emulsion for high vinyl acetate materials [3].

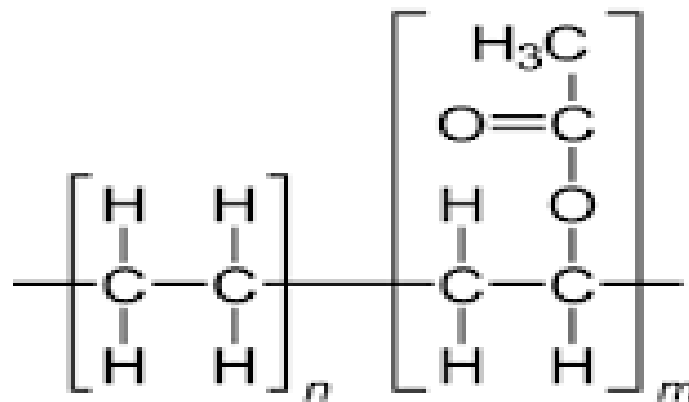


Figure 1. 1 molecular formula for EVA copolymer

EVA has been used for various applications; for making adhesives, electrical appliances, packaging, footwear industries like home-wearing sandals, shoe midsoles, and so on. EVA has good properties of waterproofness, non-toxicity, good stress-crack resistance, the resistance of UV- radiation, lightweight. This makes them familiar with our day-to-day activities. One of an EVA product which we use continuously in our life is EVA foot wears, either in sandals or in shoe's midsoles. The main problem of this polymer is its waste, which is not biodegradable and does not melt through heat. This makes EVA products difficult for recycling. To solve this problem another method is used, as an aggregate in construction works.

1.2 Statement of the problem

The problem is that, even though the addition of Ethylene-vinyl acetate (EVA) polymer improves the physical properties of cement, it retards the hydration time and decreases the compressive strength of cement which is caused by the decrease in the yield of Ca^{2+} ions which are consumed by acetate ions of EVA polymer.

Research question

- How can the yield of Ca^{2+} ion be improved?
- What will be the effect of eggshell ash on the physical properties of polymer- cement composite?

1.3 Objectives

1.3.1 General objectives

- The main objective of this thesis is to enhance hydration time and compressive strength of EVA polymer modified – cement Composites using eggshell ash.

1.3.2 Specific objective

- Investigating the performance of EVA polymer-modified cement composites with conventional cement.
- Mixing EVA polymer with cement with an accelerator of eggshell for construction application and to optimize the ratio.
- Reducing pollution which comes from the accumulation of EVA foam wastes (shoe sole /sandal/sports shoes -flip flop) which used in footwear companies, villages, trash area.

1.4 Scope of the study

The thesis includes an investigation of different Physical properties formed by the cement – polymer composites and the determination of hydration time and compressive strength of the composites. Protecting our environment from solid wastes such as; EVA products and eggshells, by using them for a construction purpose is also another aim which is covered by this thesis.

1.5 Significance of the study

This research paper has many advantages, one of its advantages is promoting improved polymer-modified cement products for different construction applications. EVA and Eggshell wastes that are used in this paper are collected from different places of our environment. So using these solid wastes for construction application helps to reduce the solid wastes, protects the environment from pollution, and also protects the soil from toxic gases. Solid waste use also decreases the use of natural materials

CHAPTER - TWO

LITERATURE REVIEWS

2.1 Introduction

Compressive strength test of cement is carried out on the cubes of Cement –sand mortar, not on a neat cement paste. This chapter covers reviews on mortar, polymers, eggshells, and related literature reviews.

2.2 Mortar

Mortar is a material which used in masonry construction to fill the gaps between the bricks and blocks. It is a mixture of sand, a binder such as cement or lime, and water. These materials are mixed as paste and set hard. Mortar bonds bricks and other units of masonry together and adheres tiles to an underlayment. Mortar provides structural integrity to the wall, floor, or other structures but is flexible enough to allow shifting without cracking.

Mortars are artificial materials produced by man for different functions including masonry, plasters, to adhere tiles, or realize decorations [4].



Figure 2. 1 Mortar

2.2.1 Types of Mortar

- i. Mud Mortar:** is a type of mortar where mud is used as a binding material and sawdust, rice husk, or cow-dung is used as fine aggregates. Mud mortar is useful where lime or cement is not available.



Figure 2. 2 mud mortar for home application

- ii. Gypsum mortar:** is made from Gypsum. This form was a mixture of plaster and sand and was quite soft.



Figure 2. 3 Gypsum mortar

- iii. Cement mortar:** is created by mixing cement with sand and water. Cement is used as a binding material and sand is used as a fine aggregate. It was popularized during the late 19th century, by 1930. It had superseded lime mortar for new construction. The main reason for this was that it sets hard and quickly, allowing a faster pace of construction. Depending on the desired strength of the cement to the sand proportion of cement mortar varies from 1:2 to 1:6.



Figure 2. 4 Cement mortar

iv. Lime mortar: is created by mixing sand, slaked lime, and water. Lime is used as a binding material and sand is used as a fine aggregate. The earliest known use of lime mortar dates about 4000BC in ancient Egypt. Its process is simple; limestone is burnt in a kiln to form quick lime. The quick lime is then slaked (mixed with water) to form slaked lime either in the form of lime putty or hydrated lime powder. This is then mixed with sand and water to form a mortar. This kind of mortar is known as non-hydraulic, sets very slowly through reaction with carbon dioxide in the air.



Figure 2. 5 Lime mortar

v. Gauged Mortar: is a type of mortar where cement and lime both are used as binding material and sand is used as fine aggregate. It is a lime mortar where cement is added to gain higher strength. The process is known as gauging. The cement to the lime proportions varies from 1:6 to 1:9. Gauged mortar is economical than cement concrete and also possesses higher strength than lime mortar.



Figure 2. 6 gauged mortar

vi. Surkhi mortar; is a type of mortar where lime uses as a binder material and surkhi is employed as fine aggregate. The surkhi is finely powdered burnt clay which provides more strength than sand and cheaply.



Figure 2. 7 Surkhi mortar for brick

vii. Modern mortar; Over 80 percent of mortars used in the UK today come from factory-produced sources as opposed to being mixed on-site. Their use reflects the ever-increasing demands for quality of building products in the development of our built environment. The factory produced mortar offers;

- Accurate cement content
- Consistent quality, strength, and color
- Reduced mixing and labor costs
- Reduced wastage
- Compliance with specifications
- technical advice and test data



Figure 2. 8 mortar in Korea

Cement mortar is a widely used building material in the world. It is a homogenous paste of cement sand and water. Different cement mortars are obtained by mixing different proportions of cement and sand. This thesis aims to improve the physical properties of polymer modified cement mortar using eggshell ash as a replacement.

2.2.2 Components of cement mortar

2.2.2.1 Cement

Cement is the World's most important building material which is used in the construction industry. It is a widely used and consumed resource on the earth. Mainly used as a binding material for the production of many structures that make up the modern World including buildings, bridges, harbors, runways, and roads. Cement used in construction are usually inorganic, often contain lime and calcium Silicate based compounds.

Cement is a finely ground of chemically combined argillaceous materials (silica, alumina) and calcareous materials (lime) with iron oxide, gypsum, and a small amount of other ingredients when mixed with water, cement sets and hardens into a solid mass upon hydration. Cement binds two or more non-adhesive substances together.

Depending on the ability of the cement to set in the presence of water, cement characterized as hydraulic or non-hydraulic. Hydraulic cement is set in wet condition and becomes adhesive due to a chemical reaction between the dry ingredients and water, for example, Portland cement. Unlikely, non – hydraulic cement does not set in wet conditions. Rather it sets as it dries and reacts with carbon dioxide in the air. After setting it is resistant to attack by chemicals. For example, slaked lime (calcium oxide mixed with water), hardens by carbonation in contact with carbon dioxide which is present in the air.

Based on the composition of materials used during its manufacture, there are various types of cement which are applied for construction purpose. For example:

- Ordinary portland cement (OPC)
- Portland pozzolana cement (ppc)

- Portland slag cement (PSC)
- Sulfate resisting Portland cement (SRC)
- Rapid hardening cement
- Quick setting cement
- White cement and so on.

Portland cement was developed from other types of hydraulic lime in England in the early 19th century by Joseph Aspdin and usually originates from limestone. Portland cement is the most common type of cement around the world as a basic ingredient of concrete, mortar, stucco, and non-special grout. It is a fine powder produced by heating limestone and clay minerals in a kiln to form clinker, grinding the clinker, and adding 2 or 3 percent of gypsum.

Composition of Portland cement:

- ✓ Lime or calcium oxide, CaO: From limestone, chalk
- ✓ Silica, SiO₂: from sand, old bottles, Clay or argillaceous rock
- ✓ Alumina, Al₂O₃: from bauxite, Recycled Aluminium, clay
- ✓ Iron Fe₂O₃: from clay, Iron ore, scrap iron and fly ash
- ✓ Gypsum CaSO₄ 2H₂O: found together with limestone

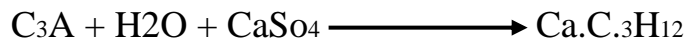
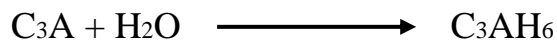
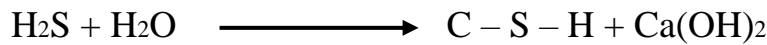
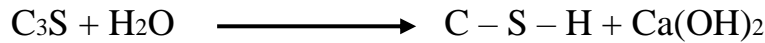
Table 2. 1 Shorthand form of portland cement

Compound	Formula	Shorthand form
Calcium Oxide	CaO	C
Silicon dioxide	SiO ₂	S
Aluminum oxide	Al ₂ O ₃	A
Iron oxide	Fe ₂ O ₃	A
Water	H ₂ O	H
Sulfate	SO ₃	S

Table 2. 2 Chemical composition of clinker

Compound	Formula	Shorthand form
Tricalcium aluminate	Ca ₃ Al ₂ O ₆	C ₃ A
Tetracalcium aluminoferrite	Ca ₄ Al ₂ Fe ₂ O ₁₀	C ₄ AF
Belite or dicalcium silicate	Ca ₂ SiO ₅	C ₂ S
Alite or Tricalcium Silicate	Ca ₃ SiO ₄	C ₃ S
Sodium oxide	Na ₂ O	N
Potassium oxide	K ₂ O	K
Gypsum	CaSO ₂ . 2H ₂ O	CSH ₂

The chemical reaction during hydration:



C – S – H - Calcium Silicate Hydrate (3CaO.2SiO₂.4H₂O)

Properties of cement compounds

- **Tricalcium aluminates, C₃A:**-It liberates a lot of heat during the early stages of hydration but has little strength contribution. Gypsum slows down the hydration rate of C₃A. Cement low in C₃A is sulfate resistant.
- **Tricalcium silicate, C₃S:**-This compound hydrates and hardens rapidly. It is largely responsible for Portland cement’s initial set and early strength gain.
- **Dicalcium silicate, C₂S:** C₂S hydrates and hardens slowly. It is largely responsible for strength gain after one week.

- **Ferrite, C₄AF:** This is a fluxing agent which reduces the melting temperature of the raw materials in the kiln (from 3,000 °F to 2,600 °F). It hydrates rapidly but does not contribute much to the strength of the cement paste.

By mixing these compounds appropriately, manufacturers can produce different types of cement to suit several construction environments.

Portland pozzolana cement (PPC) is a type of Portland cement and is the second most widely used cement in the world, next to ordinary Portland cement (OPC).

2.2.2.1.1 Portland pozzolana cement

Pozzolana is a volcanic powder found in Italy near Vesuvius. A pozzolanic material can be natural or artificial which contains silica and aluminous in a reactive form. Artificial pozzolana contains: Fly ash, silica fume, rice husk, blast furnace slug and natural pozzolana contains burnt clay, pumicite, diatomaceous Earth. This material usually doesn't possess any cementitious properties, but when it is mixed with water or moisture or lime to undergo reaction with calcium hydroxide to form compounds possessing cement properties [5].



Figure 2. 9 Portland pozzolana cement

Portland pozzolana cement is integrated pozzolana cement which is formed by synthesizing OPC cement with pozzolanic materials in a certain proportion. It is commonly known as PPC Cement. PPC is a kind of blended cement that is produced in two ways:

1. Intergrinding OPC clinker along with gypsum and pozzolanic materials in certain proportion
or

2. Grinding OPC clinker, gypsum, and pozzolanic materials separately and thoroughly blending them in certain proportions.

The most widely and commonly used cement in the world is Ordinary Portland cement (OPC). This type of cement is manufactured by mixing limestone and other raw materials which consists of argillaceous, Calcareous, and gypsum. Mostly preferred for fast construction. This cement is available in the market in three grades namely OPC 33, OPC 43, and OPC 53. These grades imply the maximum strength of the particular cement after 28 days. In PPC cement, materials such as fly ash, volcanic ash are added to OPC so that PPC is created. Hence PPC is a variation of OPC.

Nowadays, PPC is used as a substitute for OPC in many constructions.

Both PPC and OPC cement are ecofriendly, but PPC employs natural and industrial wastes which minimize industrial pollution. Based on cement grades, PPC matches OPC 33 after the process of curing. PPC has low initial strength than OPC but it hardens over time with proper curing. Based on cost, PPC is cheaper than OPC.

A. Manufacture of portland pozzolana cement

- ✓ Limestone (CaCO_2) and clay ($\text{SiO}_2\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$) are the raw materials that are used for this cement manufacture. Rocks are loaded into trucks and transported to the crushers, where crushed into fine particles.
- ✓ Fine particles of clay and limestone are fed into the air-swept ball mills in desired proportions as per requirement and mixed very well before it is sent to silos for storing.
- ✓ These mixtures are preheated up to $800^\circ\text{C} - 1000^\circ\text{C}$ where calcination of CaCO_3 to CaO takes place.
- ✓ The preheated mixture is sent into a Kiln where the mixture is heated in 1450°C in a rotary kiln. The modules formed from the burning process called clinker. The clinker is cooled by a rotary cooler.
- ✓ The clinker is now mixed with gypsum and pozzolana materials in the required proportion and thus the Portland pozzolana cement is obtained.

B. Properties of portland pozzolana cement

- The initial strength of PPC is less but the final strength is equal to the 28 days strength of OPC cement.
- Initial setting time = 30 min (minimum) and final setting time = 600min (maximum)
- It attains strength at 3 days 13MPa (minimum), at 7 days 22 MPa (minimum), at 28 days (33 MPa)
- Drying shrinkage should not be more than 0.15% and fineness should not be less than $300\text{m}^2/\text{Kg}$

C. application areas of PPC

- PPC cement is suitable to use in hostile environmental conditions. They can be utilized in the construction of marine structures, masonry mortars, and plastering, hydraulic structures. They are popularly used in mass concreting works, such as dykes, sewages pipes, dams, etc. PPC is also employed in all other applications where OPC is used.
- Used in Pre-stressed and post-tensioned concrete members
- It is used in decorative and art structures, because of its better surface finish.

D. Advantages of PPC

- Since the materials used in the manufacture are made of natural recycled wastes, it is an eco-friendly cement.
- Silica materials that are present in pozzolana make it cheap and hence reduces the cost of the cement making it economical to use.
- It is very fine cement since very good when used for plastering work.
- PPC has very good resistance against Sulphate attack, hence is used in marine structures, construction near the seashore, dam construction, etc.
- It reduces the carbon monoxide emission from the concrete making it environmentally friendly.
- Since the Pozzolano materials are very fine, they can fill gaps between the reinforcement and aggregate, thus the shrinkage, honeycomb formation, and bleeding can be reduced, which increases the strength and durability of concrete.

E. disadvantage of PPC

- Because of more fine materials, handling of concrete is difficult
- Reduction in alkalinity reduces the resistance to corrosion of steel reinforcement
- As the strength of this concrete gains slowly, any error could cause durability problems.
- The initial strength obtained is less, which affects the de-shuttering of supports early.

2.2.2.2 Sand (fine aggregate)

Sand is natural sediment of granular, mainly siliceous products of rock weathering. Particles are smaller than 2mm, are visible to the naked eye and the smallest size is 0.06mm. Sand is gritty, it has no real plasticity, and can be easily powdered by hand when dry. The most common component of sand is silicon dioxide in the form of quartz. Quartz is hard insoluble in water and does not decompose easily from the weathering processes. Streams, rivers, and wind transport quartz particles to the seashore, where the quartz accumulates as light-colored beach sand.

Sands are found around beaches, river beds, and deserts of the world. Depending on the location, sand comes in an array of colors including white, black, green, and even pink. Weathering processes such as wind, rain, and freezing /thawing cycles break down the rocks and minerals into smaller grains [6].

There are two types of sand that can be used in a mortar

1. Soft sand (builder's sand): It is a smooth kind of sand and has cohesive properties. It is used for bricklaying mortar, building foundations, paving slabs, wall rendering.
2. Sharp sand: used in concrete and can also be used for rendering walls and floors.

The function of Sand in a mortar

- Sand is used as inert material to increase the volume of mortar for the economy
- Sand offers the requisite surface area for the film of cementing materials to adhere and spread
- Sand helps to prevent mortar shrinkage and cracking of mortar during setting
- sand also used for increasing the density of a mortar

2.2.2.3 Mixing Water, Water to Cement (W/C) ratio

The material used for making a mortar is mixed with water for the following reasons:

- To cause the reaction between cement and water which results in a cement acting as a binding agent
- To make the material of mortar sufficiently plastic to be placed in position, the ratio of water to cement used in mortar affects its ultimate strength,
- For making a strong and workable cement mortar.
- To undergo hydration reaction, without water hydration reaction is not takes place.

If the mortar is too wet it will run out between the joints and weakens its ability to bond materials together. If it is too dry the bond will be weak and leads to shrinkage, creep, mound the mix, and form a depression as a result of lack of strength. The amount of water required to make depends on its material or any admixtures to improve its workability.

2.3 Reviews on Polymers

Polymers are materials made of long, repeating chains of molecules. They can be long-chain molecules or branched long-chain molecules or molecules of interconnected three-dimensional networks. A typical polymer may include thousands of monomers. Because of their large size polymers are classified as macromolecules. Polymers are used in many applications, which influence every activity of human life. They are often more economical in terms of final manufactured cost and make our life easier and colorful [7].

Polymers are known for their unreactive properties. This makes them suitable for storing food and other substances safely. But it makes it difficult to dispose of. Most polymers like poly (ethane), poly (propene) are not biodegradable. This means that microorganisms cannot break them down, so they cause a problem if disposed of carelessly.

To pursue lower density, better isolation, and other related properties, foam technology has been applied since the 1930s. Polymer foams are made up of a solid and gas phase mixed to form a foam. Ethylene-vinyl acetate foam, low-density polyethylene foam, nitrile rubber foam, polychloroprene foam, polypropylene foam, silicone foam and, etc. are some examples of polymeric foams.

Waste disposal, recyclability, flammability, and the effect of blowing agents on the environment are issues that are facing on polymer foam industry. The restriction on the use of CFCs (chloro-fluoro-carbons) has become very important in making polymer foam more environmentally friendly [3].

2.4 Classifications of polymers

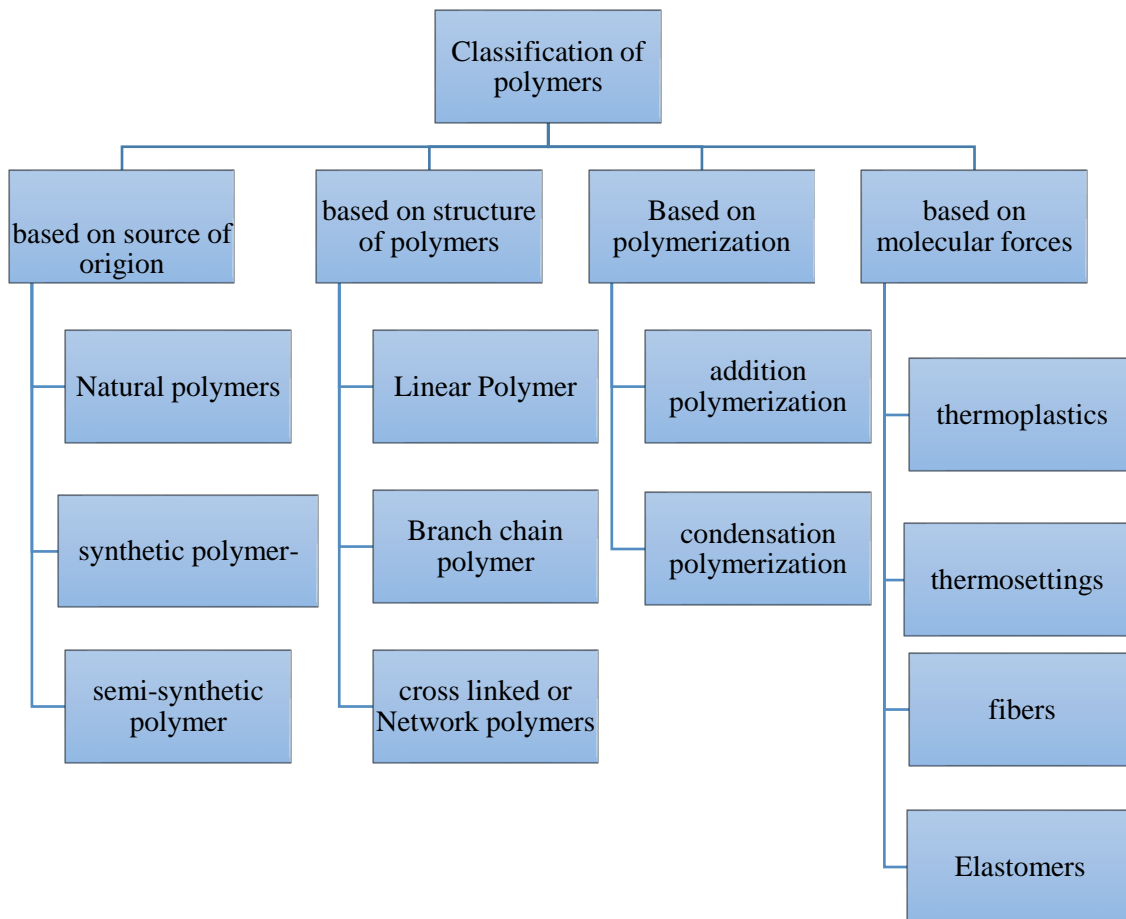


Figure 2. 10 Classification of polymers

As shown in the above figure based on molecular forces polymers classified into 4 types. Thermoplastic polymers, thermosetting polymers, fibers, and elastomers. Thermoplastics are polymers that can be softened and melted by the application of heat and solidify upon cooling. The intermolecular forces of these polymers weaken rapidly increase in temperature and yields a viscous liquid.

Most thermoplastics have a high molecular weight. As compared to Elastomers their intermolecular forces are higher but it is less as compared to fibers. They are usually linear chain polymers and can be remolded again. For example polyethylene, polyvinyl chlorides, etc.

Thermosets are polymers that are irreversibly hardened when heated. They consist of a cross-linked structure or heavily branched molecules. One of the main properties of these polymers is that they harden during the molding process and after solidifying they cannot be softened. Thermosets are brittle and tend to char and burn if heat is applied for a prolonged state. Examples include epoxy, silicone, and polyurethane, phenolic (Bakelite). Bakelite is the most common example which has relatively a poor conductor of electricity and heat.

Fibers are solids having thread-like structures possessing strong intermolecular forces like hydrogen bonding. Due to this intermolecular force of attraction, they have high tensile strength and high modulus. The strong forces lead to close packing of chains and thus impart crystalline nature. Examples are polyamides (nylon 6, 6), polyester, etc.

Elastomers

Elastomers are rubber-like solids with viscoelastic (i.e., viscosity and elasticity) properties and the polymer chains are held together by the weakest intermolecular forces. These weak polymer binding permits the polymer to be stretched. A few crosslinks are introduced in between the chains which help the polymer to retract to its original position after the force is released as in vulcanized rubber. There are two types of elastomers; unsaturated and saturated. Unsaturated elastomers are elastomers by which they can be cured with the Sulphur vulcanization process; unlikely in saturated elastomers Sulphur vulcanization cannot cure them. Some examples of unsaturated elastomers are natural rubbers (NR), polybutadiene, nitrile rubber, butyl rubber and, etc. Silicone rubber, fluorosilicate rubber ethylene-propylene rubber, and **ethylene-vinyl acetate** are some examples of saturated rubbers. Ethylene-vinyl acetate is a part of this thesis.

2.4.1 Ethylene-vinyl acetate

EVA (ethylene vinyl acetate) is the copolymer of two different monomers; ethylene monomer and vinyl acetate monomer. It is an elastomeric polymer that produces material that is “rubber-like” in softness and flexibility which makes it useful where cushioning is important such as in midsoles, sock liners, and unit soles in foot-wear. They have good low-temperature properties and are tough. EVA is popularly known as expanded rubber or foam rubber.

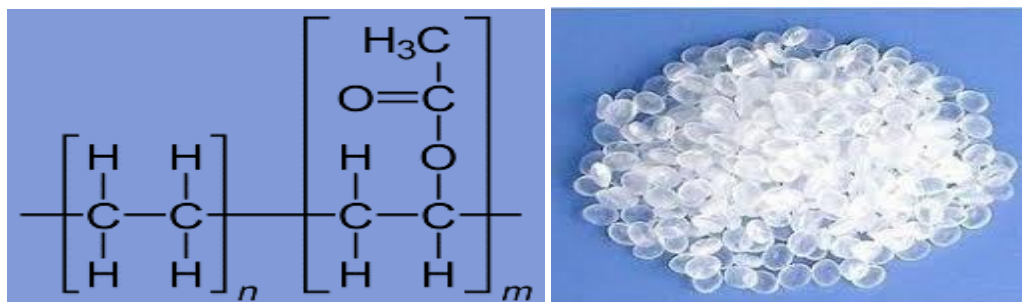


Figure 2. 11 Molecular formula for EVA

In EVA, the relative amount of vinyl acetate to ethylene influences polymer properties. The higher vinyl acetate content tends to make the polymer softer and more rubbery, while lower vinyl acetate content tends to make the polymer harder and more crystalline.

The proportion of vinyl acetate (VA) on EVA copolymer:

- the proportion of Vinylacetete approximately up to 4% is referred to as vinyl acetate modified polyethylene. It is a copolymer and processed as low-density polyethylene and some properties of polyethylene also but has increased gloss, softness, and flexibility. Typically they are non-toxic.
- Medium proportion based on the content of VA (approximately 4-30%) is referred to as thermoplastic ethylene-vinyl acetate copolymer and is a thermoplastic elastomer material. It is not vulcanized but has some of the properties of rubber or plasticized polyvinyl chloride particularly at the higher end of the range.
- EVA copolymer which is based on a high proportion of VA (greater than 60%) is referred to as ethylene-vinyl acetate rubber. It is an elastomeric polymer that produces material that

is ‘rubber-like’ in softness and flexibility. EVA has a distinctive vinegar-like odor and competitive with rubber and vinyl polymer products.

Based on the type of monomer Polymer is divided into homopolymers and copolymers. Homopolymers are formed by polymerizing only one type of monomer like polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS). Whereas copolymers are formed by polymerizing two or more than two types of monomers together like Ethylene-vinyl acetate (EVA), Acrylonitrile butadiene styrene (ABS).

Depending on the application, EVA Copolymers are manufactured in a different form:

- foam
- film
- hot melt adhesives
- wire & cable
- carpet backing
- molding & profile extrusions
- solar encapsulation, and others

2.4.1.1 EVA foam

Foam is a substance that entraps on the inside, well-dispersed bubbles/cells. Polymer foams are composed of two phases, in which a blowing agent is used to generate stabilized bubble structures inside the polymer matrix. The foaming technology has been developed and has been applied with an increasing number of different types of polymers. Polymer industry, accounting for about 10% of total commodity consumption Polyolefin foams is fourth-ranked, after polyurethane (PU), polystyrene (PS), and poly (vinyl chloride) (PVC) foams.

Polyolefin foam is one of the most important categories within polymer foams. It had first been marketed in the early 1960s and the areas of application include packaging, sports and leisure, toys, insulation, automotive, buoyancy, cushioning, and others. Soft foams made of polyolefin have a wide application, such as cushioned packaging materials, floatation materials, padding in various sports equipment as ski boots, bicycle saddles, hockey pads, boxing and mixed martial arts gloves and helmets, wakeboard boots, fishing rods and fishing reel handles, shock absorbers, and

sports shoe soles/slippers/sandals.

In terms of final foam properties, the wide range of polyolefin foams can be divided into hard foams, which are obtained using polypropylene (PP) or other high strength basic polyolefin, and softer foams, which are obtained using co-polymer, such as ethylene-vinyl acetate, EVA.

EVA foam is a closed-cell made from Ethylene-vinyl acetate and blended copolymers, it is produced under pressure by copolymerization, it has a high level of chemical cross-linking. The EVA foam made from the conventional process has a cellular structure that contains cell which is mostly closed cells (90%closed cell and 10% open cells).EVA foam is prepared by filling a preheated mold with a foamable composition, which usually contains EVA resin, a foaming agent, and cross-linking agent apply pressure to the composition and allowing foaming and curing of composition to take place. Ethylene-vinyl acetate (EVA) foam is widely used for toys, doll parts, footwear items (shoe insoles, and slippers).

A. Properties of EVA foam

The copolymer containing high levels of vinyl acetate is primarily used as a component in adhesives and coatings but can be vulcanized to obtain useful physical properties. As vinyl acetate content increases polymer flexibility, toughness, solubility in organic solvents, and clarity increase.

Table 2. 3. Properties of the homopolymers and their copolymer.

LDPE	Property	VA	EVA
910-925	Density(kg/m3)	1050-1280	930-950
122-124	Melting point(0C)	-	47-100
-	Softening temp(0C)		
150-600	Elongation at break (%)	10 - 20	300-750
22-31	Tensile strength(mPa)	29.4-49	15-28
10*10 ⁻⁵	Thermal expansion coeff(K-1)	7-22*10 ⁻⁵	16-25*10 ⁻⁵

I. physical properties of EVA foam

- Density nominal value at 230C 940-960 kg/m^3 according to ASTM D150.
- The material has good clarity and gloss.
- EVA foam is softer and more resilient than PE foam.
- Hot-melt adhesive.
- Light-weight.
- High Resistance for electricity
- Good processability.
- Weather-resistant and can be washed in dishwashers.
- Yellow and red-colored products are however more likely to decolorize due to UV radiation.
- High viscosity.
- High molecular weight.
- Easy to form and allow great design flexibility
- Waterproof properties.
- Resistance to UV radiation.
- Acoustic and thermal insulation properties.
- Buoyancy with low water absorption.
- Suitability for thermo-forming and thermo-molding.
- EVA is cheaper compared to natural rubber.
- The density of Ethyl Vinyl Acetate at 200-500 kg/m .

II. Mechanical properties of EVA foam

The mechanical properties of EVA foams depend not only on the base polymer and their cellular structure. The composition of EVA foam also makes changes its properties.

- An Increase in VA content leads to a decrease degree of crystallinity,
- An Increase in VA content leads to increase polarity.

- Decrease Degree of crystallinity leads to decrease melting Temp-decrease chemical resistant-decrease surface hardness.
- A Decrease Degree of crystallinity leads to decrease stiffness modulus.
- Decrease Degree of crystallinity leads to increase impact resistant.-increase friction factor.
- Increase Degree of polarity leads to increase compatibility with other polymers-increase adhesion -increase printing ability.

High amounts of EVA will produce a harder material with different mechanical properties than foams with a lower amount of EVA.

III. chemical properties of EVA foams

The structure of EVA foam plays a major role in its broad use. The gas bubbles in the EVA foam have a closed-cell structure. Because of the closed cell structure, EVA foam has unable to absorb fluids. Unlike this, sponges are made of a material with an open-cell structure which allows them to absorb fluids.

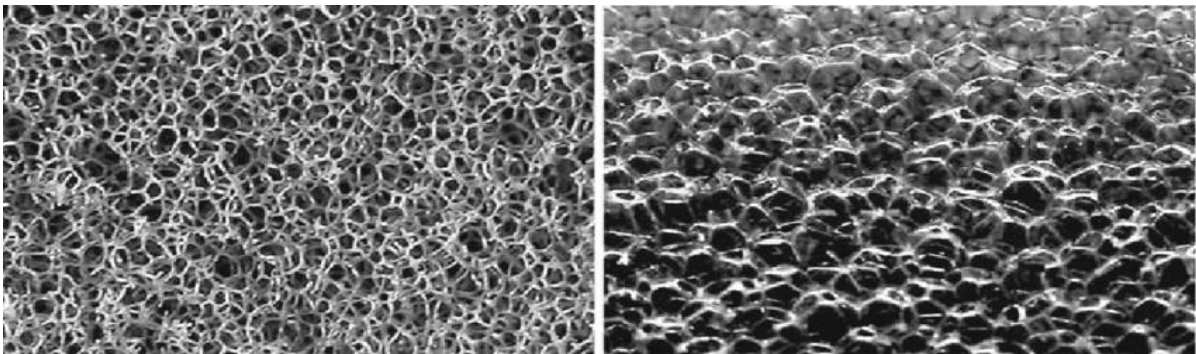


Figure 2. 12 Microstructure of Open cell (left) and closed-cell (left) foams

According to Weight % Vinyl acetate, EVA Copolymer has the following products;

- Very low EVA 1- <7%:** commodity films, e.g., Bakery bags, ice bags, frozen food bags, overwrap, and fresh produce wrap.

- ii. **Low EVA 7-< 17%:** blow molding, foam applications, extrusion /lamination, injection molding, industrial stretch wrap, and wire and cable.
- iii. **Mid EVA 17 -< 25%:** extrusion coating, injection molding, lamination film, heat-seal layers, hot melt adhesives, agricultural films.
- iv. **High EVA 25 – 35%:** carpet backing, hot melt adhesives, injection molding, wax blended coatings, extrusion, solar panels, and photovoltaic cells.
- v. **Ultra-high EVA 36-45%:** hot melt adhesives, coating, polymer modification, grafted polymers.

B. Advantages of EVA foam

- They will not be wet when we sit in it after it has rained.
- The material is dirt-repellent and easy to clean. Dirt cannot build itself in cells because they are closed.
- The smooth surface makes it easy to clean the material. There is no need to post-process the material to make it dirt-repellent and is easy to clean. This factor makes an EVA foam a hygienic material.
- Creating a texture on the material is another benefit of this polymer.
- EVA foam is resistant to chemicals, most alkaline bases, oils, and acids.
- EVA foam is resistant against chemicals, most alkali basis, oils, and acids
- EVA is competitive with rubber.
- They are soluble in a wide range of aliphatic, aromatic, and chlorinated solvents
- It has a distinctive ‘vinegar’ odor
- EVA has good resistance to oils and fuels.

C. The disadvantage of EVA foam

During the formation of the material, chemical connections are created, which are not easily broken. Once the material is formed heating the material will not melt it, but it will burn. because of this, the material is not recyclable.

Ethylene-vinyl acetate (EVA) is one of lightweight garbage, for example, slippers, sport shoe sole, plastic cones. etc. These EVA products make EVA foam Environment unfriendly material.

Alvarez et al (2008), outlined the following disadvantages of Human Health and Environmental concerns for EVA foam.

- EVA Produces toxic chemicals in fires.
- Uses carbon monoxide in production.
- Risk of fire due to pellets or powder plastic.
- Chloride catalyst is used in some vinyl acetate production.
- Risk of children choking from small parts due to product breakage
- Incomplete combustion produces carbon monoxide and low molecular weight aldehydes.
- Environmental Concerns from Ideal disposal method is in a landfill.
- Byproducts of ethylene production.

Application of EVA polymer

- In biomedical engineering applications as a drug delivery device
- wire/cable insulation,
- packaging film,
- adhesives/coatings,
- Carpet backing, sandals, sports shoe soles, sports leisure, sound damping sheets.
- for artificial flowers
- bicycle saddles
- ski boots
- Fishing rods and etc.



Figure 2. 13 Application of EVA wastes **a.** EVA nutrition bags **b.** EVA rubber cable **c.** Laminated EVA hot melt adhesive film **d.** EVA packaging film **e.** EVA for screen printing **f&g** EVA foot wears (for sandals and soles) **h.** EVA foam vehicle

2.4.1.2 EVA WASTE PROBLEM

According to the study of lemma, 2007 the increase of solid waste generations resulted from rapid urbanization and the increase in population numbers. The amount of solid waste in Addis Ababa and other fast growing areas in the country has been increasing over time, largely attributed to rapid growth population rate [8].



Figure 2. 14 solid wastes in Jimma around keyafer

After the end use of this footwear, some of the communities use them as firewood. The firing of EVA produces toxic chemicals which are dangerous for our breathing system and others reject them to landfills, riverbanks, market areas, on-street, behind their houses, in available open areas, in trashes and, etc.

Although these EVA products are useful materials for the footwear industry, they have become an environmental concern because of their poor biodegradability. EVA goes through an anaerobic decomposition process called thermal degradation (polymer changes its properties under the influence of increased temperature) that often occurs in landfills resulting in the release of Volatile organic compounds (VOCs) into the air. VOCs contribute to the formation of tropospheric ozone, which is harmful to humans and plant life. Thermal degradation of EVA is Temperature-dependent and Occurs in two stages; in the first stage, acetic acid is lost and followed by the degradation of unsaturated polyethylene polymer.

EVA, which is used in the manufacture of foot wears results in serious environmental pollution of groundwater and rivers when disposed to landfills. They can take thousands of years to naturally degrade.

2.4.1.3 Recycling of EVA wastes

Polymeric materials have the highest growth rate in the world. One of these materials is EVA foam which is widely used for shoe midsoles, sandals, etc. EVA cannot be melted through the heat because of its molecular chains they do not decompose easily. So, another recycling process is needed.

Since the 1970s polymer additives have been widely studied for a construction purpose; as a means of improving the properties of cement. These polymer – cement composites offer significant advantages over conventional cement in terms of strength, elasticity, adhesiveness, water tightness, chemical resistance, waterproofing capacity, and freeze-thaw resistance. In this thesis paper, EVA wastes are used as an aggregate for masonry works.

2.4.2 Eggshell wastes

An eggshell is the outer covering of a hard-shelled egg and some forms of eggs with soft outer coats. Eggshell waste is a solid waste, with a production of several tons per day. Eggshell is mostly sent to the landfill with a high management cost. It is economical to transform the eggshell waste to create new values from these waste materials. Eggshells are a rich source of mineral salts, mainly calcium carbonate, which corresponds to about 94% of the shell. Layer farms produce large amounts of shells, whose final disposal poses a challenge from the environmental standpoint [9].



Figure 2. 15 egg shell wastes

2.5 Related Literature reviews

Our world population number increases from time to time very fastly. The growing urbanization creates ever-increasing needs for high buildings. Cement is one of the main essential materials needed for constructing those buildings. Some buildings, bridges collapse in a short period of time. As we see in our country Ethiopia, the crack will be made too early. The cause for the collapse may be bad design, faulty construction, foundation failure, lack of strength, or maybe a natural disaster. Regarding to strength, cement plays a major role.

The most familiar cement in the world is Portland cement. It has high compressive strength but has less tensile and flexure strength. To improve these properties most researchers studied by modifying the cement with polymer, but this also causes a decrease in compressive strength. So, we need an accelerator to enhance the hydration rate as well as compressive strength. Let us see some literature views:

A researcher has been conducted to the ethylene/vinyl acetate (EVA) copolymer, it had used like latex or powder, is added to mortars and concrete to improve the fracture toughness, impermeability, and bond strength to various substrates. The physical and chemical interactions were already proved after one day of hydration but during the first hour just the physical interaction was identified and some evidence of chemical interaction. The work aimed to evaluate the chemical interaction between EVA and Portland cement during the first hours of hydration in the thermogravimetric analysis. EVA added two percentage 5% and 10% to modified cement paste or blended Portland cement with 10% calcareous filler was used, according to Brazilian Standard (CPII F 32). This work leads to the following conclusions: EVA copolymer reduced the calcium hydroxide in the cement paste due to the chemical interaction between Ca^{2+} ions and anions acetate, released in the EVA alkaline hydrolysis. This interaction was verified at the first 15 *min* by the absence of the dehydration peak in thermos gravimetric analyses until 5 and 6 *h* in EVA-modified pastes with 5% and 10% EVA, respectively; the new peak observed at 380 °C, referred to the first calcium acetate decomposition and, the increase in CO_2 release, due to its calcium carbonate formed during the decomposition of the calcium acetate. This chemical interaction probably decreases the EVA flexibility, thus promoting the elasticity modulus of cement-based materials increases [10].

The second researcher studied the microstructural tests for EVA modified cement pastes and he concluded that: There is evidence of chemical interaction of acid groups released by alkaline hydrolysis of EVA with Ca^{2+} ions in the pore water of the cement pastes. The products of this interaction are calcium acetate and polyvinyl alcohol. Calcium acetate is an organic salt with high hygroscopicity, and polyvinyl alcohol is water-soluble. These two factors can impair the performance of EVA-modified mortars and concretes when saturated by water. EVA copolymer changes into a polymer formed by ethylene, vinyl acetate, and polyvinyl alcohol.

EVA retards the whole cement hydration reactions and leads to the formation of Hadley's grains and big rods. The quantity of calcium hydroxide in cement pastes is decreased also because EVA consumes Ca^{2+} ions from the solution. EVA-modified cement pastes showed the expressive formation of a polymeric film deposited on the surface of anhydrous and hydrated cement phases, and also partially lining pore walls. The results showed that the acetate groups of EVA copolymer undergo alkaline hydrolysis and interact with Ca^{2+} ions of the pastes to form an organic salt (calcium acetate). The calcium hydroxide content is decreased, the crystals appear to be well-formed and many Hadley's grains were observed. A calcium-rich, porous and hexagonal structure phase was detected, probably due to an acetic-acid attack on calcium hydroxide crystals [11].

The other researcher conducted the effect of replacement of various percentages of industrial EVA waste as aggregate for the production of lightweight concrete for construction application. He concluded that: Compressive strength of concrete at the age of 7 and 28 days decreased with increased amounts of EVA waste for cube test and concrete blocks.

The density of concrete decreased with increased amounts of EVA waste. That means the concrete molded with EVA presented lower levels of bulk density of fresh concrete in comparison to the concretes with natural aggregates. The weight of concrete decreased with increased amounts of EVA waste. This is useful in applications requiring non-load-bearing lightweight concrete, such as hollow concrete blocks. Increased value of slump with increased amounts of EVA waste. The cost of lightweight concrete blocks mixed with EVA waste was not so high price compared with the general concrete blocks without EVA waste. Water absorption was increased by increasing the amount of EVA waste. That made the EVA concrete block easy to be used as plaster and mortar. Reduced pollution comes from the accumulation of EVA foam waste that is used in footwear

companies according to the quantities of EVA waste which used in the mix design of concrete blocks when used concrete Block without EVA waste. The permeability decreased with the increase in replacement percentage of EVA waste. Reduced consumption of electricity/energy which used for mixing the composite Concrete because EVA waste had low density, compared to general concrete which had high density for natural aggregate[3].

Another researcher used X-ray transmission microscopy to observe the effect of EVA on the early hydration of C_3S and C_3A . The result showed that EVA particles agglomerate around the hydrating C_3S grains, and act as nucleation agents in the development of the composite microstructure. EVA inhibited or even prevented the formation of ettringite crystals during the early stage of hydration, and resulted in a cloud of small, bright particles concentrated around the hydrating C_3A grains [7].

Another researcher investigated that polymers added to cement to enhance its physical properties can retard its hydration reaction and reduces its compressive properties. This investigation into the delayed hydration of polymer– cement composites containing varying amounts of the polymer ethylene-vinyl acetate yielded the following; increasing the ratio of polymer to cement reduces the yield of Ca^{2+} ions generated owing to an increase in viscosity, and this delays hydration in polymer– cement composites.

During the hydration of cement–polymer composites, vinyl acetate in ethylene-vinyl acetate is hydrolyzed and acetate ions are produced that react with Ca^{2+} ions to generate calcium acetate. Moreover, as the Ca^{2+} ions are consumed by this process, the unreacted Sulphate ions left behind delay hydration. These two factors represent the mechanism by which early hydration is delayed in cement–polymer composites [2].

The above paper reviews show that the addition of polymer to a cement mainly results in a reduction in compressive strength and retardation in the hydration reaction. This thesis targets to reduce this problem by the addition of eggshell ashes as an accelerator. Reviews written below show that a high amount of calcium carbonate gives better strength and improved setting time to cement material.

Because of extra calcium oxide in an eggshell, the addition of eggshell ashes has been established as a good accelerator for a cement material. This thesis concludes that the eggshell ash content will increase the strength of properties of the cement stabilized matrix up about 35% on average. That shows the usage of eggshell ash as an additive will increase the strength of the concrete [12].

According to Mtalib et al. (2009), the addition of eggshell ash to the ordinary Portland cement decreases the setting time of the cement. They conclude that the eggshells ash is used as an accelerator in concrete because the higher content of the calcium oxide leads to the faster rate of setting [13].

Another research studied an experimental investigation of eggshell powder (ESP) addition influence on the Portland cement mortar performance. Two different eggshell powders states were prepared. These include untreated eggshell powder (UESP) and treated eggshell powder (TESP). The TESP consists of heating the ESP to 750 C for one hour in an electric furnace. Cement mortar of ordinary Portland cement with (1:3), (cement to sand) ratio, were mixed with each of two ESP states (UESP and TESP) at different percentages ranged from (0 to 20) wt% of the total weight of the cement mortar mixture. Water absorption, thermal conductivity, compressive strength, and hardness properties are measured for the mortar samples after curing for (28 days). The results generally showed that the addition of ESP to the cement mortar improved its properties. The addition of TESP to mortar mixture gave better properties as compared to the UESP addition at the same weight ratio. The water absorption percentages of the samples were decreased by about 30% at 15 wt% addition of TESP. The compressive strength of the mortar was increased by 29% over the control mortar at 15 wt% addition of TESP. The hardness values of mortar are slightly enhanced with increasing ESP ratio, which increased by about 2.5% at 20 wt% addition of TESP. The better thermal insulation of mortar samples was obtained from the addition of UESP, reaching the rate of reduction in the thermal conductivity to 40% than the control mortar [14].

Based on composition both eggshell and cement have the same chemical composition, which is calcium compound. Results from setting time show that by adding eggshell ash to cement the setting time of cement decreases. In short the higher amount of eggshell ash the faster rate of setting and apply to all percentages of eggshell ash that were used in the investigation [15].

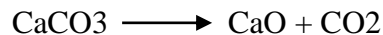
The addition of eggshell powder transformed ettringite to monosulfoaluminate and to monocarboaluminate. In 20% eggshell powder, the formation of monocarboaluminate was detected in the early stages and accelerated the hydration reaction. The CaCO_3 from the eggshells reacted with the C3A and changed the hydration products of the pastes. The addition of eggshell powder provided nucleation sites in the hydration products and accelerated cement hydration [16].

The addition of eggshell ash to the concrete mix increases the strength of the concrete. In short, the higher percentage of eggshells ash in the mix means a higher compressive strength for the concrete. Hence, it is suggested that eggshell ash can be used as a partial cement replacement in concrete [17].

Another experimental study was carried out to study the workability and compressive strength of M40 grade concrete incorporating Eggshell Powder (ESP) as supplementary cementitious material, to reduce the cement content in concrete. ESP was ground into two fineness (50 μm and 100 μm) and three different percentages (5%, 10%, and 15% by weight of cement) of ESP was used to replace cement content. It was observed that partial cement replacement using ESP was successful in achieving higher strength compared to the control sample. It was determined that 10% ESP was optimum, where the highest compressive strength was achieved. Furthermore, the fineness of ESP also influenced the compressive strength, the ESP which passed 50 μm resulted in better strength. The optimum ESP to be utilized was determined to be 10% in both fineness [18].

Two researchers studied the influence of the presence of concrete admixtures on the hydration reaction of cement pastes. Two admixtures (1) an accelerator and (2) a retarder, have been added to the cement pastes at different ages. The presence of such admixtures affects the physicochemical properties of the products. The addition of the accelerator the rate of hydration reaction whereas the retarder delays the reaction rate; the intensity of X-ray increases diffraction peaks characterizing the formed phases during the hydration reaction is generally increased in the presence of the accelerator and reduced with the retarder [19].

Calcination of calcium carbonate yields calcium oxide and carbon dioxide.



From the above literature reviews, we can conclude that the addition of EVA polymer to a cement reduces compressive strength and retards the hydration time, opposite to this addition of Egg shells increases the compressive strength and reduces the setting time. The existing gap in this literature is on the addition of polymer that reduces compressive strength and retards hydration time, to minimize the gap this research incorporates eggshell ash with polymer-modified cement.

The target of this paper is to study the effect of an eggshell on hydration time and compressive strength of polymer modified cement mortar. Based on the above literature reviews this study expects an improved hydration time and compressive strength of polymer modified –cement composites.

CHAPTER - THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter contains a description of EVA and eggshell waste for the beneficial reuse in construction and component materials of mortar mixes. EVA and eggshell wastes are selected based on availability in Ethiopia and its difficult recycling of EVA. The experimental work was conducted at Jimma, Jimma institute of technology, in the department of civil and environmental engineering, construction material laboratory, and Material science and engineering laboratory.

3.2 Study area

This study was conducted at Jimma town, southwestern Ethiopia, from February 2020 to March 2021. Jimma is locally known as the town of Abba Jiffar. It is located 354kms far from Addis Ababa on the highway of Mettu - Gambella at an altitude of 1620 m.a.s.l. Geographically, the town is located at 70 40’N latitude and 360 60’E longitudes. According to the master plan of the town, the total area of land of the town is 4623 (46.23km²) hectares[8]. All the laboratory works are conducted at Jimma institute of technology.

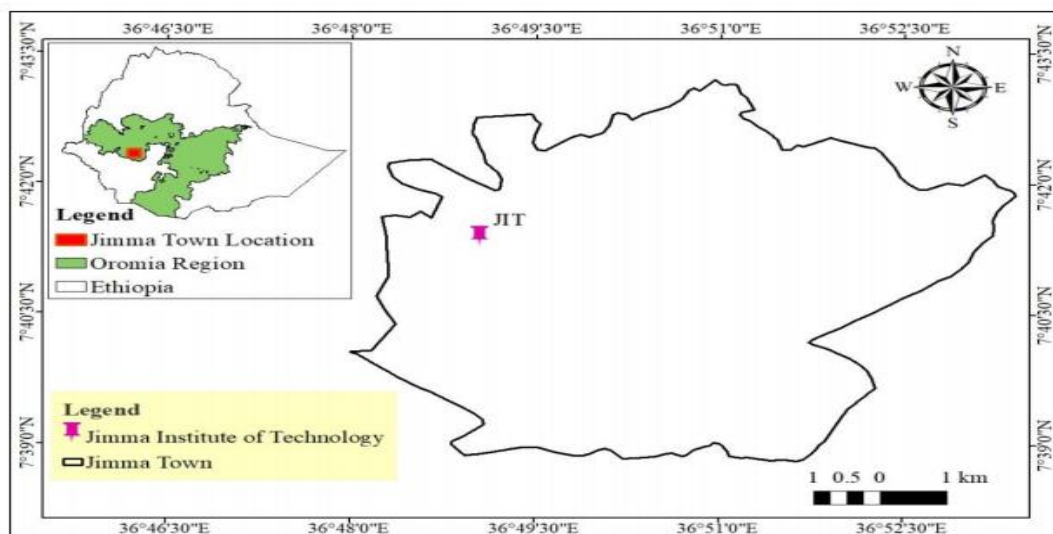


Figure 3. 1 Map from GIS (ground information system)

3.3 Materials used

The materials used in this paper are EVA waste aggregates, Portland pozzolana cement, sand, eggshell ash, and water.

3.3.1 Preparation of EVA waste (EVA aggregate)

Based on the 2007 census conducted by the central strategy agency, the Jimma zone has a total population of 2,486,155 and 521,506 households. Out of this, Jimma town has a population number of 120,960 with 32,191 households which results in an average of 3.76 persons to a household and 30,016 housing units [8]. It is common to see EVA slippers on a road, around the play station, waterway area, corner of a man’s house/corner of the fence and so many places. To find out the total number of waste slippers, data was collected from 20 households randomly with different living standards.

Table3. 1 Slipper wastes in Jimma town

#	Total number of family	No. of slipper wastes (piece)
1.	6	3
2.	3	4
3.	4	2
4.	7	4
5.	4	2
6.	8	4
7.	5	2
8.	5	3
9.	3	1
10.	4	2
11.	7	2
12.	4	3
13.	3	2
14.	5	2
15.	6	3

16.	7	4
17.	4	1
18.	5	1
19.	6	3
20.	2	2
Total		50
Average		2.5

The above data estimates that each household has 2.5 slipper wastes annually. As mentioned before based on a census of CSA data of 2007 shows that the total number of households in Jimma was 32,191, so to find a total number of slipper wastes 32,191 is multiplied by 2.5 which gives 80,477.5 pieces of wastes are throughout randomly.

For this study, EVA waste which is mainly slipper (sandals) is obtained by collecting from local villages like individual houses, street, and waterway areas as shown in fig 3.1. EVA wastes were cut into pieces of different lengths using a scissor and sieved with a sieve diameter of (2mm-6mm). EVA aggregates are used to replace 5% of fine aggregates.



Figure 3. 2 EVA slipper wastes



Figure 3. 3 Fraction of EVA wastes before cutting and after cutting

3.3.2 Preparation of eggshell

The eggshell was collected from different restaurants. The egg shell is been dry under the sun for a period of three or four days and burns locally using an Electric injera pan. The burned ash is been taken to a grinding machine and ground to powder. The eggshell ashes were sieved with $75\mu\text{m}$ sieve according to ASTM c 136 and all materials that passed through were taken for usage [20].



Figure 3. 3 preparation of eggshell ash

3.3.3 Portland pozzolana cement (PPC)

Portland pozzolana cement equivalent ASTM 150 from Dangote cement factory with grade 32.5R is used.

3.3.4 Fine aggregates (sand)

The sand used for experimental work was locally available sand found in Jimma as per the ASTM c 136 standards [20]. The sand sieved through a 2.3 mm sieve to remove any particle greater than 2.3mm then washed to remove any dust.

3.3.5 Mix design for a mortar

- The materials used in this work are PPC, EVA waste, Eggshell ash, and fine aggregate (sand), the tests were carried out on a 0.65 water-cement ratio. firstly cement and fine aggregate (sand) were manually mixed in a ratio of (1:3) for 3 minutes then water was added and all materials were mixed according to ASTM C270-10[21]. This pure mix without EVA and eggshell is called a control sample.
- The percent replacement of fine aggregate is calculated by replacing 5% of fine aggregates with EVA aggregates, next 15%, 30%, 45% & 60% of EVA aggregates are replaced by eggshell ash. This was done to determine the proportion that would give the most favorable result. The 0% replacement was to serve as a control for 5% replacement of fine aggregates with an EVA and 5% replacement was also to serve as a control for other samples which is finally used for comparison. Samples of mortar mixes were prepared and tested in Civil and environmental engineering laboratories at Jimma institute of technologies (JIT), construction of material laboratories.

The mix proportions studied for EVA waste mortar are shown below:

Table 3. 2 Mix proportions for a mortar

Mass of Quantities							
Samples	Cement (Kg)	Fine agg.(Kg)	EVA= (5% of sand)	EVA(Kg)	ESA = (% of EVA)	ESA(Kg)	Water(Kg)
S1	0.558	1.674	0%	-	0%	-	0.363
S2	0.558	1.590	5%	0.084	0%	-	0.363
S3	0.558	1.590	5%	0.0714	15%	0.0126	0.363
S4	0.558	1.590	5%	0.0588	30%	0.0252	0.363
S5	0.558	1.590	5%	0.0462	45%	0.0378	0.363
S6	0.558	1.590	5%	0.0336	60%	0.0504	0.363

EVA = 5% of sand

ESA = 15%, 30%, 45%, & 60%, of EVA

ASTM C127-10 standard was used for mix design for mortar cubes, test, the cube specimens have the standard size (100mm ×100mm × 100mm) were cast for mortar as shown in fig. below. After 24 hours the specimens were de-molded and cured for 7 and 28 days and tested [21].

Table 3. 3 Mix proportion for setting time of cement

Mass of Quantities						
Samples	Cement (Kg)	EVA (%)	EVA (Kg)	ESA (%)	ESA (Kg)	Water (Kg)
S1	0.3	0%	-	0%	-	0.1
S2	0.3	5%	0.045	0%	-	0.1
S3	0.3	5%	0.038	15%	0.007	0.1
S4	0.3	5%	0.032	30%	0.014	0.1
S5	0.3	5%	0.025	45%	0.02	0.1
S6	0.3	5%	0.018	60%	0.027	0.1

EVA (%) = replacement of (x) percentage of sand,
 Cement: sand (1:3) \implies 0.3Kg (cement) = 0.9Kg (sand)
 EVA (%) = 5 % (0.9Kg) = 0.045Kg
 ESA (%) = replacement of (y) percentage of EVA



Figure 3. 5 cube test for mortar mixes

3.4 Methods

3.4.1 Determination of the initial and final setting time

I. Consistency test

The normal consistency of hydraulic cement refers to the amount of water required to make a neat paste of satisfactory workability [22]. The determination of the correct amount of water is required for the reason that the rate of hydration and setting of cement is affected by the water to cement ratio. This test method is intended to be used to determine the correct amount of water required to prepare hydraulic cement pastes for testing [23]. It is determined using the Vicat Apparatus. This apparatus measures the resistance of the paste to the penetration of a plunger of the needle of 200gm released at the surface of the paste [22].

Apparatus used: Vicat apparatus, Weighs and weighing device, Graduated Cylinder, Mixing Dish, and Trowel were used to perform the test.

Test procedure: A 400gm of cement sample is carefully mixed with a measured quantity of clean water for 3min. Using a trowel, quickly form the cement paste in the approximate shape of a ball by tossing 6 times from one hand to another through a free path of about 6in (150mm) to produce a neatly spherical mass that may be easily inserted into the Vicat ring mold, immediately after filling the mold, level the paste and lower the plunger gently, and bring it in contact with the surface of the paste, tighten the screw setting the movable indicator to the upper zero marks of the scale and release the plunger immediately, thirty seconds after releasing the plunger record its penetration, the paste said to be of normal consistency when the rod settles 10+ or -1mm below the original surface within thirty seconds, repeat the above procedures varying the proportion of water until a paste of normal consistency obtained, The amount of water required for normal consistency then expressed as a percentage weight of the dry cement.

$$\% \text{Water} = \frac{\text{Weight of water in gm}}{\text{Weight of cement in gm}} \times 100 \quad \text{Eq.3. 1}$$

Hence, the usual range of water-cement ratio for normal consistency is between 26% and 33% [22].



Figure 3. 6 consistency test

II. Setting time

These testing methods define the time of setting of hydraulic cement using a Vicat needle[24]. The cement forms a solid and hard mass when mixed with water upon hydration. This phenomenon is known as the setting of cement. The duration a cement paste requires to undergo setting is its setting time. As the setting is the consequence of hydration of cement, it is affected by the amount of water used to prepare cement paste, i.e. water-cement ratio. Cement pastes with different water-cement ratios will, generally, have different setting times but it is the setting time of cement paste with normal consistency [22].



Figure 3. 7 test for setting time

There are two types of set times to be determined in the laboratory:

- i. Initial setting time:** This is regarded as the time elapsed between the moments that the water is added to the cement up to the time that the paste starts losing its plasticity or the duration of cement paste related to 25mm penetration of the Vicat needle into the paste in 30 seconds after it is released.
- ii. Final setting time:** Is the time elapsed between the moment at which the water is added to the cement and when the paste has completely lost its plasticity and has attained sufficient firmness to resist certain definite pressure. This means the time that related to zero penetration of the Vicat needle into the paste.

Apparatus used: Vicat apparatus, weighing balance, Mixing dish or Tray, Stopwatch, Graduated cylinder, Trowel, and Hand glove.

Test procedure: Prepare a neat 300gms of cement paste by gauging the cement with 0.85 times the water required to give a paste of normal consistency. Start a stop-watch at the instant when water is added to the cement. Insert the paste into the conical ring and remove the excess with a sharpened trowel. Invert the larger ring on the glass plate and cut off the excess paste on the smaller end with a sharpened trowel. Immediately after molding, allow the sample to stay in the moist room for 30 minutes after molding without disturbing. Lower the needle gently until it comes in connection with the surface of the test specimen. Release the rod quickly & allow it to penetrate the paste for 30seconds. Determine the dispersion of the 1mm needle at this time and every 15min thereafter until penetration of 25mm or less is gained. The time between the initial contact of cement and the penetration of 25mm is the initial time of setting. The final setting time: - is determined by replacing the needle for the Vicat apparatus with the final set needle, which has an annular attachment at the end. The final setting time is when the needle does not bowl visibly into the paste [22].



Figure 3. 8 apparatus for workability test

3.4.2 Workability of a mortar

Workability is the ease with which mortar can be handled while placing it.

Apparatus: Balance, graduated cylinder, molds, flow table apparatus and flow mold, trowel mixing dish.

Procedure: prepare sand and water with a given proportion, mix cement and sand for about a minute (dry mix) and add the required amount of water and mix for about two minutes, carefully wipe the flow tabletop clean and dry then place the flow mold at the center of the table, fill the mortar to the mold with three layers and tamp 25 times each layer with a tamping rod. The tamping pressure shall be just sufficient to ensure uniform filling of the mold, cut off the mortar to a plane surface, and slush with top of the mold, by drawing the straight edge of the trowel, wipe the tabletop clean and dry being especially careful to remove any water from around the edge of flow mold, lift the mold away from the mortar then drop 25 times within 15 sec. through a height of 13mm, using caliper determines the flow by measuring the diameter of the mortar along the lines on the tabletop (take 4 readings).

According to ASTM standards, the mortar is said to be workable if the sum of four diameters is between 95 to 100mm [22].

3.4.3 Determination of compressive strength

Compressive strength is the most essential test because it gives an indication of the mechanical strength of hardened mortar, the compressive strength was determined after 7 and 28 days, 3 cubes

the test for each period, and the average is reported as the compressive strength. The mortar cube was tested by applied axial loads on the area of the cube face ($100 \times 100 \text{ mm}^2$).

Apparatus used: Testing machine, apparatus for making mortar (mold, mixing dish fine aggregates, cement EVA aggregates ESA, water), Tamping road (having a cross-section of 13 by 25 mm and convenient length of 120-150 mm).

Procedure: Immediately following completion of flow tests return the mortar from the flow table to mix dish. Quickly scrape the mixed dish sides and then remix the entire batch for 15 sec, start molding the specimens within the total elapsed time of 2 min and 30 sec. After completion of the original mixing of the mortar batch (molds should be oiled to easily demold the specimen), fill the mortar into the cube mold with three layers and tamp each layer 25 times with tamping road. The tamping pressure shall be just sufficient to ensure uniform filling of the mold, after 24 hours remove the mortar cubes from the mold and cure them in water, determine the compressive strength of mortars at 7 and 28 days [22].



Figure 3. 9 compressive strength test machine

$$P = \frac{F}{A} \quad \text{Eq.3. 2}$$

Where; P= applied pressure (MPa)

F= crushing load (N)

A= Area of specimen in contact with load (mm^2)



Figure 3. 10 compressive strength test and its output

3.4.4 Characterization technique

3.4.4.1 X-Ray Diffractometer

X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material [25].



Figure 3. 11 X-Ray diffractometer

Knowledge of the microstructure of hydrated cement is essential for Forecasting their performance. One of the most important techniques for characterizing cementitious materials is X-Ray Diffraction (XRD). Both cement producers and cement Researchers have made extensive use of X-Ray Diffraction (XRD) to identify and quantify the crystalline phases inground cement [26]. In this study, XRD is used to identify the crystalline phases of $\text{Ca}(\text{OH})_2$ in hydrated cement.

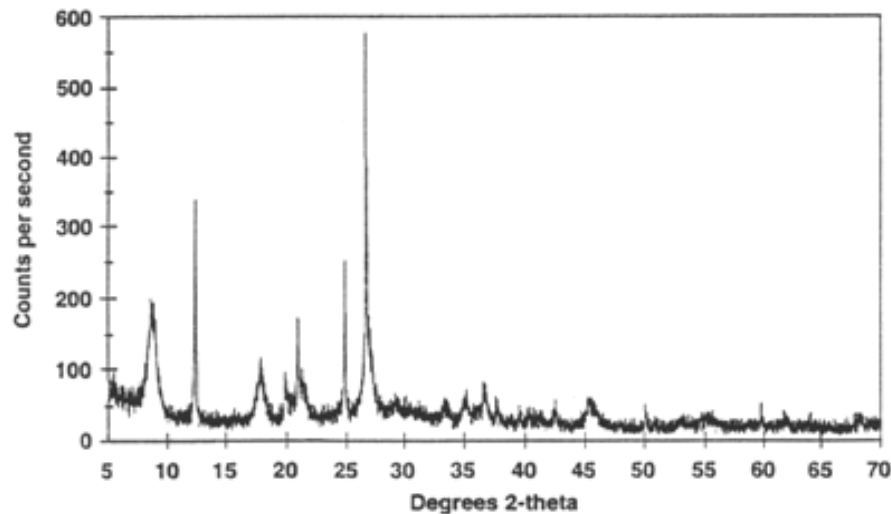


Figure 3. 12 Sample diffractometer output (<https://serc.carleton.edu/18400>)

Sample preparation

Good sample preparation plays an important role in accurate measurement and obtaining a good diffraction pattern as the sample is analyzed by its crystallographic properties using X-Ray powder diffraction. A good sample preparation ensures us three main things,

- A result matching the reality
- Minimization of diffraction errors
- A good statistical representation

Sampling

The materials used for this experiment are Portland pozzolana cement (PPC), Ethylene-vinyl acetate (EVA), and eggshell ash.

Critical steps;

- Sampling

- Grinding
- hydration stoppage
- Storage

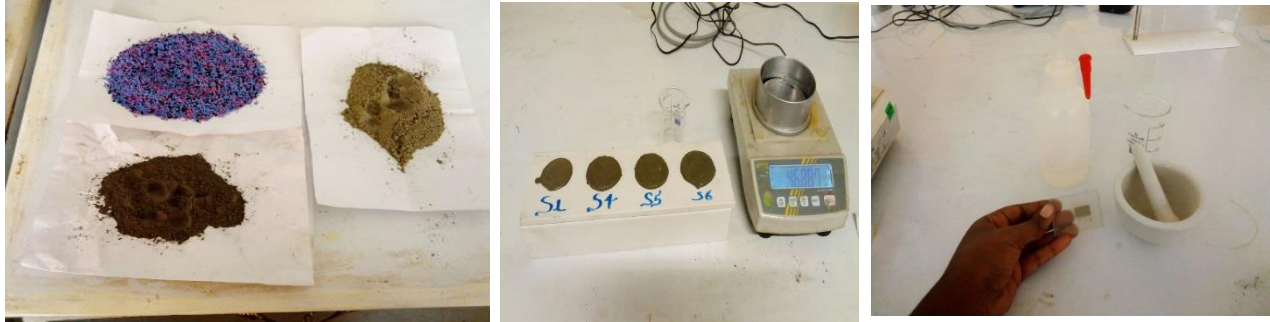


Figure 3. 13 Sample preparation for XRD test

An EVA polymer is ground to a smaller size, and eggshell ash and PPC cement are sieved with a 20 μm sieve. Six samples (Cement only, cement with EVA polymer and 15%, 30%, 45%, 60% of eggshells to polymer - cement composite) are prepared with different ratios. Each sample was mixed with distilled water by hand for 2 min. at the water to cement ratio (W/C) of 29.5% and cast for 24 hours. After 24 hours the sample will be ground and hydration stoppage will occur. Then the sample was immersed in acetone for 3 days and followed by vacuum drying to remove the solvent. After 3 days the samples are stored on the dry surface, then the sample is placed in the diffractometer, and an XRD pattern is acquired.

CHAPTER - FOUR

RESULT AND DISCUSSION

4.1 Introduction

The results of Setting time, compressive strength, average density, and XRD characterization are stated and discussed to evaluate the optimum replacement percentage of ESA on polymer-modified cement composites.

4.2 Consistency test result

The water to cement ratio affects the rate of hydration and setting of cement. So, the determination of the correct amount of water is highly required. Hence, the usual range of water-cement ratio for normal consistency is between 26% and 33%.

Table 4. 1 Observed normal consistency test result

Trials	Wt. of cement (gm)	W/C ratio	Amount of Water (ml)	Penetration Depth(mm)
1	400	0.26	105	8.5
2	400	0.29	115	9.32
3	400	0.295	118	10

Finally, the observed test result shows that the penetration depth of 8.5mm, 9.32mm, and 10mm when the water-cement ratio was 0.26 (26%), 0.29(29%), and 0.295(29.5%) respectively. Hence, the normal consistency of cement was found 10mm at the 3rd trial when the water-cement ratio was 0.295(29.5%) which is between the limited range (10 ± 1 mm). Therefore, the result shows that the water demand for this cement is moderate. This means it requires medium water to prepare a paste of satisfactory workability (normal consistency).

4.3 Setting time result

The setting time was conducted for 6 samples and the result is given in the table below.

Table 4. 2 Observed setting time for Sample 1 (S₁)

Tri al	Cement (gm)	Water(ml)	w/c ratio	T ₀	T1	T2	Initial setting time(T3)	Final setting time(T4)
1	300	100.3	0.295	2:30	180	195	188.6(min)	316.2(min)
Penetration depth(mm)					26.2	24.1		
2	300	100.3	0.295	2:30	165	180	182(min)	280(min)
Penetration depth(mm)					28.7	23.8		
3	300	100.3	0.295	2:30	174		185(min)	312(min)
Penetration depth(mm)					25			
Average setting time							185.2	302.7(min)

Where:

T₀ = Time in an hour at which water is first added to the cement

T1 = Time in a minute at which the needle penetrates the paste to a depth of 26.2mm.

T2 = Time in a minute at which the needle penetrates the paste to a depth of 24.1mm.

T3 = Time in a minute at which the needle penetrates the paste to a depth of 25mm.

Which was computed by **interpolation** for S₁ as follow:

$$180 = 26.2\text{mm}$$

$$X = 25\text{mm}$$

$$195 = 24.1\text{mm}$$

$$X = 188.57 \text{ minute}$$

T4 = Time at which the final set needle makes only an impression (i.e. D=0).

The initial setting time of the cement was 188.57minutes = 3:14(3 hr. and 14 minutes).

The final setting time can be estimated by the equation:

$$\text{Final setting time (in minutes)} = 90 + 1.2 \times (\text{Initial setting time})$$

$$= 90 + 1.2 \times (188.57) = 316.2 \text{ minutes} = 5:27(5 \text{ hrs. and } 27 \text{ minute})$$

Finally, Ethiopian Standard recommends that the initial setting time for cement not be less than 45 minutes and the final setting time not exceed 10 hours [22]. Herein, the initial setting time of this cement is more than 45 min and the final setting time of this cement was not more than the recommended time (10hr).

The rest samples (S2, S3, S4, S5, & S6) data are written in the appendices.

Table 4. 3 Summary of initial and final setting time of polymer modified cement

Samples	Initial Setting time	Final setting time
S1	185.2	302.7
S2	261.2	403.3
S3	247.2	386.6
S4	240.7	378.8
S5	230.7	366.8
S6	222.1	356.5

From table 4.8 results, the substitution of ESA to a polymer-modified cement decreases the setting of cement. ESA has been indicated to have an accelerating effect on the setting of polymer modified cement. From the percentage decreases in the initial and final setting times presented in Table 4.8 and plotted in Figure 4.7, it can be seen that the higher the contents of ESA in the polymer - cement paste, the faster the setting of the cement. For all the percentage contents of ESA used, both the initial and final setting times satisfy the requirements of Ethiopian standard(Dinku 2002)[22]. Ethiopian standard recommends that the initial and final setting times of Cement should not be less than 45 minutes, and not greater than 10 hours, respectively. It can also be observed that ESA has a similar decreasing effect on the initial and final setting times of cement. This similar effect is being that the decrease in the setting time of polymer-modified cement between successive percentage substitutions of ESA is generally gradual for the initial setting time as well as for the final setting time. The decrease in the setting time of the polymer-modified cement due to the addition of ESA portrays ESA as an accelerator. Therefore, ESA can be used to advantage as a substituent in polymer modified cement mortar.

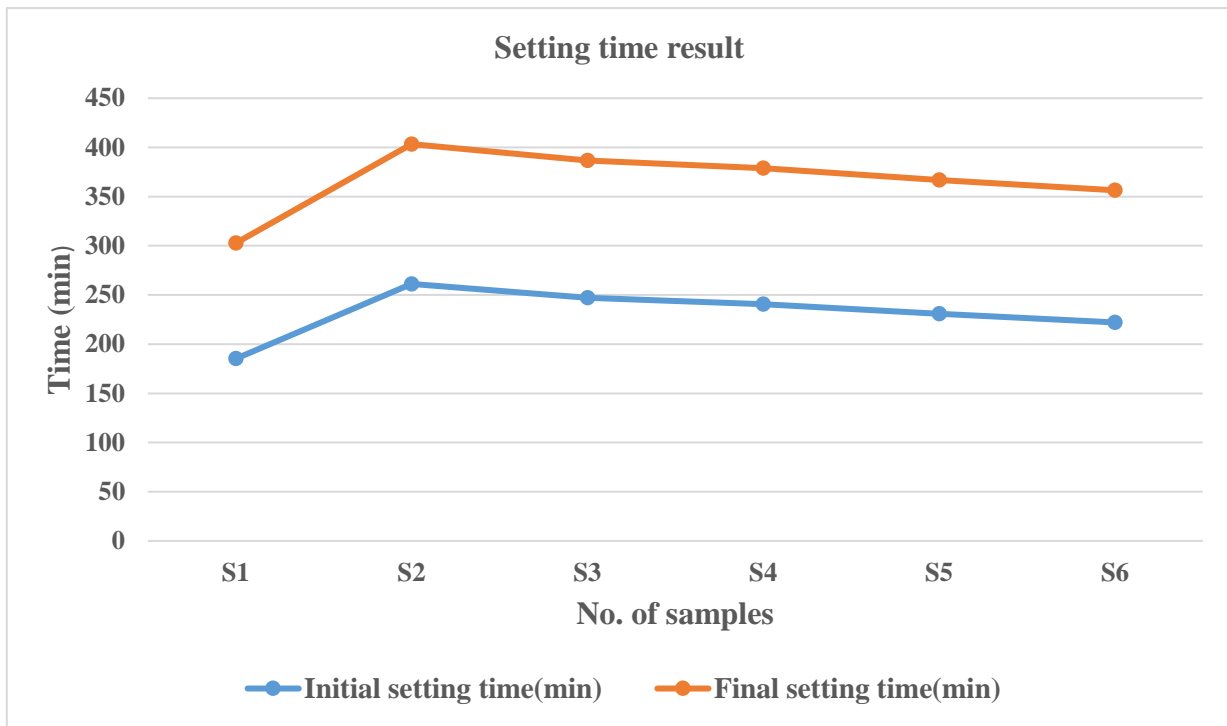


Figure 4. 1 Summary of initial and final setting time of polymer modified cement

4.4 Average density and weight of Mortar mixes

The weight was measured for cubes taken from a water tank. The value of densities obtained with different percentages is shown in table 4.3 below for the 0.65 W/C ratios.

Table 4. 4 Density of polymer-modified cement mortar test result

Samples	Volume (m ³)	Weight (Kg)		Density (Kg/m ³)	
		7 th day	28 th day	7 th day	28 th day
S ₁	0.001	2.000	1.983	2000	1983
S ₂	0.001	1.693	1.660	1693	1660
S ₃	0.001	1.723	1.713	1723	1713
S ₄	0.001	1.753	1.720	1753	1720
S ₅	0.001	1.783	1.750	1783	1750
S ₆	0.001	1.796	1.780	1796	1780

$$Density = \frac{\text{Average weight of mortar sample}}{\text{Volume of a sample in m}^3} \quad \text{Eq.4. 1}$$

It is found from the unit weight of there is replacing EVA aggregate results in a considerable decrease in unit weight when compared with control mortar (blank) and replacing an ESA with a different percentage increases the unit weight when compared to the Polymer modified cement mortar. For the accuracy of the result, each sample is cast three times and tested and an average of three is taken for the accuracy of results. The results of densities of mortar are shown in table 4.4 and fig 4.2 according to the formula:

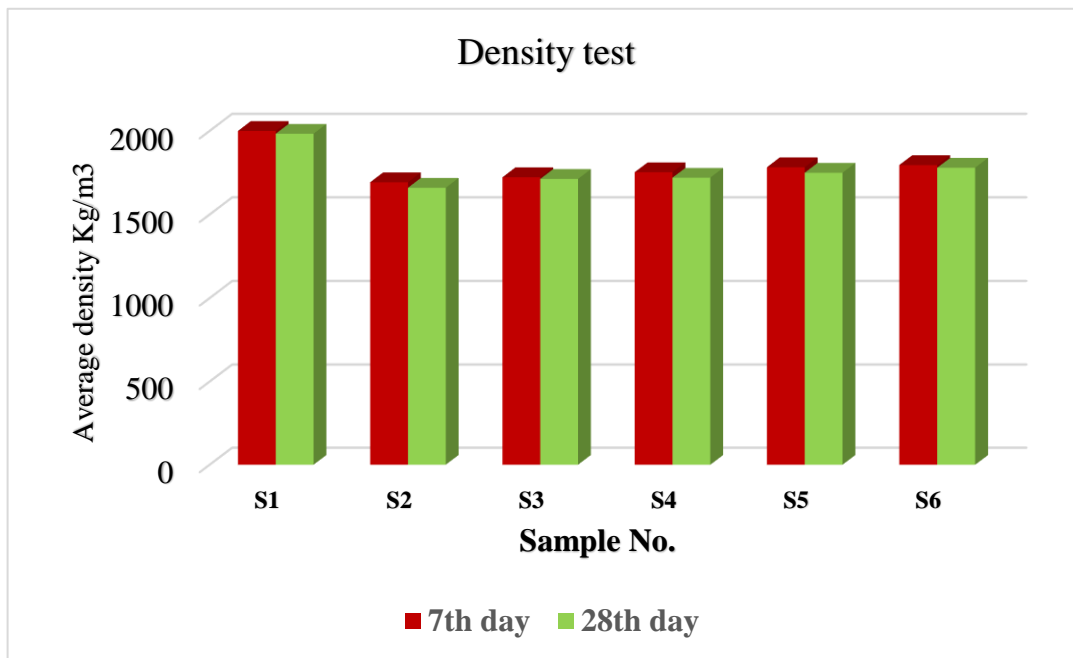


Figure 4. 2 Density of Polymer-modified cement mortar

4.5 Workability test result

Table 4. 5 Workability test for sample 1.

Reading	Diameter in (mm)
1.	23.1
2.	24.5
3.	25
4.	23.9
total	96.5mm

Table 4. 6 Workability test for all samples

Samples	Average diameter in (mm)
S ₁	96.5
S ₂	94
S ₃	94.9
S ₄	95
S ₅	95.5
S ₆	96

According to ASTM standards, the mortar is said to be workable if the sum of the four diameters is between 95 and 100, so the water to cement ratio of 0.65 for mortar cubes fulfills ASTM standard except for S₂ and S₃.

4.6 Compressive strength test

The Compressive strength of mortar mixtures is determined at the 7 and 28 days for the samples S₁, S₂, S₃, S₄, S₅, and S₆. There were three samples for each test and the average result will be taken. The effect of age of Mortar mix and Proportions of ESA waste on a compressive strength can be observed from table 4.14 – 4.18.

In table 4.7 observe the values of average strength for a control sample of 7th and 28th days is 9.65 and 13.95 MPa, respectively. Results for S₂, S₃, S₄, S₅, and S₆ are given in appendices.

Table 4. 7 Observed compressive strength test result for sample 1 (control sample)

No	Test Age (days)	Dimensions (m)			Volume (m ³)	Weight (kg)	Failure Load (kN)	Comp. Strength (MPa)	Unit weight of mortar (kg/m ³)
		L	W	H	L*W*H				
1	7 th	0.10	0.10	0.10	0.001	2.01	103.56	10.36	2010
2		0.10	0.10	0.10	0.001	2.0	94.46	9.45	2000
3		0.10	0.10	0.10	0.001	1.99	91.57	9.16	1990
Mean						96.53	9.65		
1	28 th	0.10	0.10	0.10	0.001	2.0	142.3	14.23	2000
2		0.10	0.10	0.10	0.001	1.98	138.45	13.85	1980
3		0.10	0.10	0.10	0.001	1.97	137.63	13.76	1970
Mean						139.46	13.95		

Table 4. 8 Summary of Compressive strength test result for all sample

Samples	Compressive strength N/mm ² (MPa)	
	7 th day	28 th day
S1	9.65	13.95
S2	3.39	6.5
S3	3.82	6.95
S4	4.13	7.15
S5	4.32	7.55
S6	4.84	7.87

Table 4.8 presented that the control mortar (S_1) obtained the highest reading among mortar specimens in the compressive strength test which is 9.65 MPa and 13.95 MPa at the age of 7 and 28 days respectively, while polymer modified mortar (S_2) obtained the lowest reading which is 3.39 MPa and 6.5 MPa at the same age. Replacing 15% of ESA (S_3) in polymer modified cement achieved improved compressive strength which is 3.82 MPa and 6.95 MPa at the same ages. As the percentage of ESA replacement increases as shown in S_4 , S_5 , and S_6 , readings of the strength test is also increases. The replacement of 60 % of eggshell ash obtained the highest reading among polymer modified mortar specimens which is 4.84 and 7.87 MPa at the age of 7 and 28 days respectively. Therefore, Replacing Eggshell ash with polymer-modified cement is a better way to have the highest compressive strength.

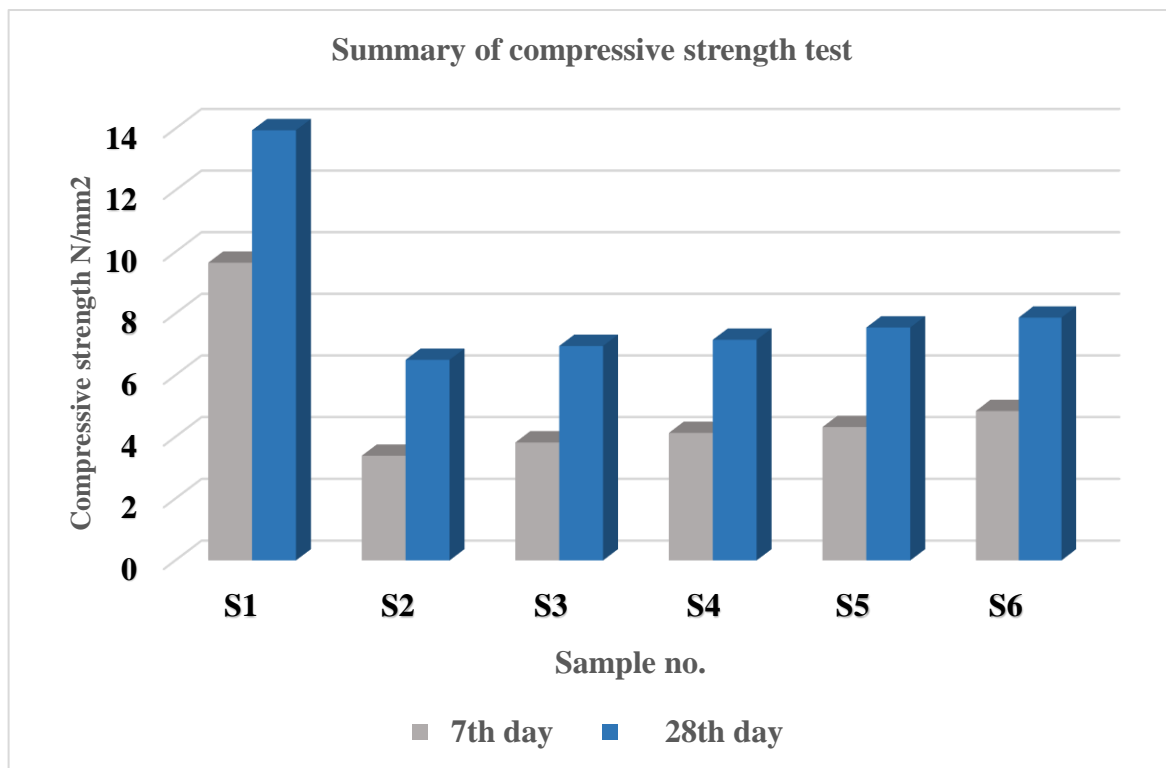


Figure 4. 3 Summary of compressive strength test result

4.7 XRD analysis

XRD analysis of the hydrated cement compounds is reported below. Two-phase are showed in the result, Ca_3SiO_5 and $\text{Ca}(\text{OH})_2$. The standard data obtained from an Expert high score plus showed that Calcium silicate (Ca_3SiO_5) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) has a monoclinic and hexagonal crystal system, with the space group of P and P-3m1, respectively. Each peak in the XRD gave us information about the lattice parameter, which can be obtained from the d-spacing and miller indices.

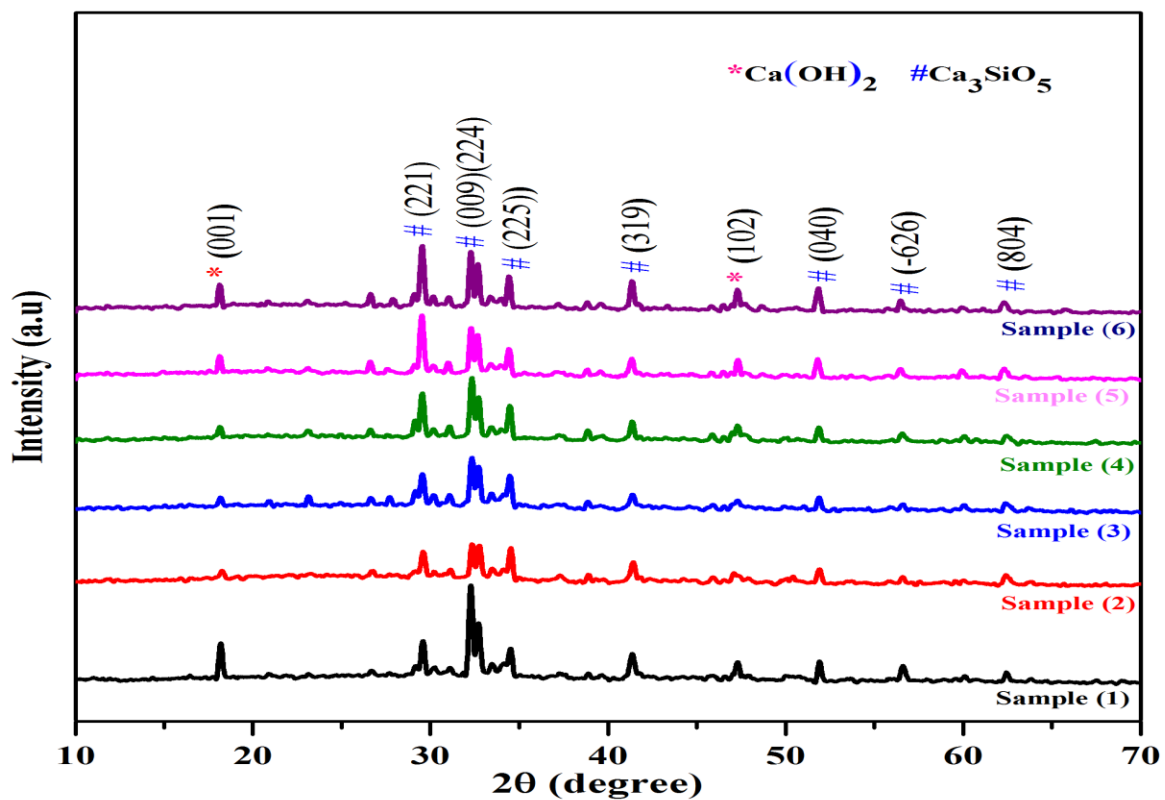


Figure 4. 4 X-ray diffraction pattern for $\text{Ca}(\text{OH})_2$ after 24 hours

The XRD result is shown in fig 4.1 above was conducted for 6 different samples, Sample1 (S_1 .) for cement only, S_2 . Cement-polymer (In the previous discussion for compressive strength 5% of sand is replaced by polymer for modification, in this experiment, 5% of sand values of polymers are added on cement), S_3 , S_4 , S_5 , S_6 corresponds to a polymer to Eggshell ash (P-ESA) ratios of

15%, 30%, 45%, 60%, respectively. From the XRD results shown in the above figure, the Intensities of the peaks of Ca(OH)_2 at $2\theta = 18$ and 47 degrees are plotted against different ratios. The calcium ion which is generated in cement reacts with hydroxide ion, if the polymers are added the calcium ion reacts with COO^- (acetate ion) in the acetate group of polymer structure, that is why the intensity of Ca(OH)_2 peak decreases as shown in sample 2. From sample 3 up to sample 6, eggshell ash which is added to polymer-cement composite helps to increase the intensities of Ca(OH)_2 as shown in fig 4.4 above. This is due to the high content of calcium ions that are presented in an eggshell.

CHAPTER - FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

According to the laboratory tests conducted to investigate the effect of replacement of various percentages of an eggshell waste for the production of polymer modified cement mortar for construction application, the conclusions obtained from different tests are summarized as follows:

- Substitution of ESA to a polymer-modified cement decreases the setting of cement. ESA has been indicated to have an accelerating effect on the setting of polymer modified cement. The higher the content of the ESA, the greater the accelerating effect.
- Compressive strength of polymer modified mortar at the age of 7 and 28 days increased with increased amounts of Eggshell ash for cube test of a mortar.
- The density and weight of a polymer-modified cement mortar increased with increased amounts of ESA as compared to pure polymer-modified mortar.
- Reduced pollution which comes from the accumulation of EVA foot-wear wastes and eggshell wastes in different places of our environment.

5.2 Recommendations

The use of EVA waste in a mortar mix is a new development in the world, so, it needs a lot of studies before this material is used in construction. Based on the result of the study performed in this research the following recommendations can be made;

- Using EVA waste with a diameter below 2mm for the mortar mixes needs further study. EVA wastes with smaller sizes may have a good result on their properties.
- Using EVA waste other than ‘slippers’ needs further study.
- The Effect of eggshell powder on a polymer-modified mortar also needs another study.

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APPENDICES

APPENDIX A

I. Quantity of cement, sand, EVA, ESA for cement-mortar cube test

Mix proportion of cement to sand (1:3)

Dimension of a cube $0.1\text{m} * 0.1\text{m}$

Total volume = $(0.1 * 0.1 * 0.1) * n = x$

Hardened total volume = $(1.5 - 1.6) * x$
 $= 1.55x = y$

Where, n = number of moulds

x = Total volume

(1.5-1.6)- For shrinkage and wastage of mixes

Total mix ratio = $1+3 = 4$

Cement quantity = $1/4 (y) = z$

Unit weight of cement = $1440\text{Kg}/\text{m}^3$

Mass of cement = volume of cement * density of cement
 $= z * 1440 \text{ Kg}$

Mass of sand = $3 * \text{Mass of cement}$

Mass of EVA = 5% (mass of sand)

Mass of ESA = 15%, 30%, 45%, 60% (mass of EVA)

Water to cement ratio (w/c) = 0.65

w = $0.65 * \text{mass of sand (Kg)}$

APPENDIX B

II. Observed setting time result for S₂, S₃, S₄, S₅, & S₆

Table 4. 9 Observed setting time for sample 2 (S₂)

Tri al	Cement (gm)	Water (ml)	w/c ratio	T ₀	T1	T2	Initial setting time(T3)	Final setting time(T4)
1	300	100.3	0.295	2:30	250	265	262.2(min)	404.6(min)
					Penetration depth(mm)			
2	300	100.3	0.295	2:30	255.3		255.3 (min)	396.4(min)
					Penetration depth(mm)			
3	300	100.3	0.295	2:30	266.2		266.2(min)	409.4(min)
					Penetration depth(mm)			
Average							261.2(min)	403.3(min)

Table 4. 10 Observed setting time for sample 3

Tri al	Cement (gm)	Water (ml)	w/c ratio	T ₀	T1	T2	Initial setting time(T3)	Final setting time(T4)
1	300	100.3	0.295	2:30	243	252.6	246.7(min)	386.1(min)
					Penetration depth(mm)			
2	300	100.3	0.295	2:30	239	247	246.4(min)	385.7(min)
					Penetration depth(mm)			
3	300	100.3	0.295	2:30	248.3		248.3(min)	387.9(min)
					Penetration depth(mm)			
							247.15 (min)	386..6 (min)

Table 4. 11 Observed Setting time for sample 4

Tr ial	Cement (gm)	Water (ml)	w/c ratio	T ₀	T ₁	T ₂	Initial setting time(T ₃)	Final setting time(T ₄)
1	300	100.3	0.295	2:30	241.5		241.5(min)	379.8(min)
2	300	100.3	0.295	2:30	238.2	244.3	240.3(min)	378.4(min)
3	300	100.3	0.295	2:30	240.3		240.3(min)	378.3(min)
Average							240.71	378.8(min)

Table 4. 12 Observed Setting time for sample 5

Tr ial	Cement (gm)	Water(ml)	w/c ratio	T ₀	T ₁	T ₂	Initial setting time(T ₃)	Final setting time(T ₄)
S₁	300	100.3	0.295	2:30	234.5		234.5(min)	371.4(min)
S₂	300	100.3	0.295	2:30	227		227(min)	362.4(min)
S₃	300	100.3	0.295	2:30	225	232	230.7(min)	366.8(min)
							230.7(min)	366.8(min)

Table 4. 13 setting time result for sample 6

Tr ial	Cement (gm)	Water (ml)	w/c ra- tio	T ₀	T1	T2	Initial setting time(T3)	Final setting time(T4)
S₁	300	100.3	0.295	2:30	215	223	220.7(min)	354.84(min)
S₂	300	100.3	0.295	2:30	222	228	225.5(min)	360.6(min)
S₃	300	100.3	0.295	2:30	218	221	220(min)	354(min)
Average							222.06(min)	356.48(min)

APPENDIX C

III. Observed compressive test for S2, S3, S4, S5, & S6

Table 4. 14 compressive strength test for sample 2 (S2) with 5% of EVA waste

No	Test Age (days)	Dimensions (m)			Volume (m ³)	Weight (kg)	Failure Load (kN)	Comp. Strength (MPa)	Unit weight of mortar (kg/m ³)
		L	W	H	L*W*H				
1	7 th	0.10	0.10	0.10	0.001	1.69	33.85	3.39	1690
2		0.10	0.10	0.10	0.001	1.69	34.93	3.49	1690
3		0.10	0.10	0.10	0.001	1.70	32.99	3.29	1700
Mean							33.92	3.39	
1	28 th	0.10	0.10	0.10	0.001	1.67	68.70	6.87	1670
2		0.10	0.10	0.10	0.001	1.64	60.27	6.03	1640
3		0.10	0.10	0.10	0.001	1.67	66.12	6.61	1670
Mean							65.03	6.50	

Table 4. 15 compressive strength test for sample 3 (S3) with 15% of ESA

No	Test Age (days)	Dimensions (m)			Volume (m ³)	Weight (kg)	Failure Load (kN)	Comp. Strength (MPa)	Unit weight of mortar (kg/m ³)
		L	W	H	L*W*H				
1	7 th	0.10	0.10	0.10	0.001	1.73	38.95	3.90	1730
2		0.10	0.10	0.10	0.001	1.72	37.11	3.71	1720
3		0.10	0.10	0.10	0.001	1.72	38.46	3.85	1720
Mean							38.17	3.82	
1	28 th	0.10	0.10	0.10	0.001	1.72	70.13	7.01	1720
2		0.10	0.10	0.10	0.001	1.71	69.27	6.93	1710
3		0.10	0.10	0.10	0.001	1.71	68.99	6.90	1710
Mean							69.46	6.95	

Table 4. 16 compressive strength test for sample 4 (S4) with 30% of ESA

No	Test Age (days)	Dimensions (m)			Volume (m ³)	Weight (kg)	Failure Load (kN)	Comp. Strength (MPa)	Unit weight of mortar (kg/m ³)
		L	W	H	L*W*H				
1	7 th	0.10	0.10	0.10	0.001	1.78	41.32	4.13	1780
2		0.10	0.10	0.10	0.001	1.75	42.15	4.22	1750
3		0.10	0.10	0.10	0.001	1.73	40.35	4.04	1730
Mean							41.27	4.13	
1	28 th	0.10	0.10	0.10	0.001	1.71	73.12	7.31	1710
2		0.10	0.10	0.10	0.001	1.73	71.3	7.13	1730
3		0.10	0.10	0.10	0.001	1.72	70.2	7.02	1720
Mean							71.51	7.15	

Table 4. 17 compressive strength test for sample 5 (S5) with 45% of ESA

No	Test Age (days)	Dimensions (m)			Volume (m ³)	Weight (kg)	Failure Load (kN)	Comp. Strength (MPa)	Unit weight of mortar (kg/m ³)
		L	W	H	L*W*H				
1	7 th	0.10	0.10	0.10	0.001	1.80	44.41	4.44	1800
2		0.10	0.10	0.10	0.001	1.77	43.85	4.39	1770
3		0.10	0.10	0.10	0.001	1.78	41.19	4.12	1780
Mean							43.15	4.32	
1	28 th	0.10	0.10	0.10	0.001	1.76	75.13	7.51	1760
2		0.10	0.10	0.10	0.001	1.75	76.97	7.70	1750
3		0.10	0.10	0.10	0.001	1.74	74.5	7.45	1740
Mean							75.53	7.55	

Table 4. 18 compressive strength test for sample 6 (S6) with 60% of ESA

No	Test Age (days)	Dimensions (m)			Volume (m ³)	Weight (kg)	Failure Load (kN)	Comp. Strength (MPa)	Unit weight of mortar (kg/m ³)
		L	W	H	L*W*H				
1	7 th	0.10	0.10	0.10	0.001	1.79	48.42	4.84	1790
2		0.10	0.10	0.10	0.001	1.78	49.33	4.93	1780
3		0.10	0.10	0.10	0.001	1.82	47.45	4.75	1820
Mean							48.4	4.84	
1	28 th	0.10	0.10	0.10	0.001	1.78	79.56	7.96	1780
2		0.10	0.10	0.10	0.001	1.79	80.23	8.02	1790
3		0.10	0.10	0.10	0.001	1.77	76.44	7.64	1770
Mean							78.74	7.87	

