Addis Ababa University

Addis Ababa Institute of Technology (AAiT)

School of Multi-Disciplinary Engineering

Center of Materials Engineering (CME)

Enhancing the Cracks-Resistant Behavior of Concrete Materials: Combined effects of TiO_2 Nanoparticles and Waste Plastics Fiber

By

Belete Balta

Addis Ababa, Ethiopia

June, 2020

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Advisor

Dawit Gemechu (PhD)

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Declaration

I hereby declare that the work which is being presented in this thesis entitled "Enhancing the crack-resistant behavior of concrete materials: combined effects of TiO_2 nanoparticles and waste plastics fiber" was composed by myself, with guidance of my advisor, the work contained herein is my own, has not been presented in whole or in part, for any other degree or professional qualification.

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Belete Balta,

Addis Ababa,

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Abbreviations

TNP	Titanium dioxide Nano-Particles
WPFs	Waste Plastic Fibers
HPC	High Performance Concrete
CCMs	Conventional Concrete Materials
MSE	Materials Scientist and Engineer
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
C-S-H	Calcium silicate hydrate
CH	Calcium hydroxide,
NF	Nano-filler
OPC	Ordinary Portland Cement
CA	Coarse Aggregate
FA	Fine Aggregate
NSC	Nano Scale Cracks
C_3S	Tricalcium Silicate
C_2S	Dicalcium Silicate
C_4AlF	Tetra calcium Alumino-ferrite
NSM	Nano Scale Material
NS	Nano Silicon
SP	Super-Plasticizer
CaO	Calcium oxide
$CaCO_3$	Calcium carbonate, limestone
CO_2	Carbon dioxide gas
MONP	Metal Oxide Nanoparticle

Measurements

Gt	Giga tons
Mt	Metric tons
Kg	kilogram
cm	centimeter
mm	millimeter
gm.	gram
Wt. %.	Weight percentage
^{o}C	Celsius degree

Abstract

Experimental investigation of the combined effects of TiO_2 Nanoparticles (TNP) and Waste Plastic Fiber (WPF) for the modifications of concrete materials has been conducted. The TNP partially substituted cement by the wt. % of (0, 0.5, 1.0, and 1.5) and WPF partially substituted sand by the wt. % of (0, 0.2 and 0.4) in C-25 grade concrete. The strength for modified and unmodified concrete after 3, 7, and 28 days of curing has been tested. The results showed that the maximum strength and durability were achieved by combined effects in comparison to all other concretes for all the curing days. The SEM analysis of concrete modified with both WPF and TNP showed a densified and well-compacted microstructure than unmodified and also only TNP modified concrete. The XRD analysis of concrete modified with both WPF and TNP showed the existence of more phases, which are responsible for strength modification than only TNP modified and unmodified concrete. Furthermore, the thermal analysis of the samples was conducted with DSC-TGA (Differential Scanning Calorimetry-Thermo-Gravimetric Analysis). The maximum weight loss was recorded for unmodified concrete at lower temperatures than modified concrete. The problems associated with conventional concrete materials with respect to a maximum load resistance, compressive strength and splitting tensile strength, and crack-resistant behavior has been modified. Achieving high strength, gaining high quality, and long term serviceability were critical issues to Ethiopian construction sectors and in other countries as well. In this study, the combined effects of TNP and WPF addressed the challenges of concrete cracking and durability properties.

Keywords: Nanomaterials, TiO_2 Nano-particles, Cracks-Resistant Behavior, Durability, Mechanical-Strength

Chapter One: Introduction

1.1. Background of the study

Concrete is commonly used and major construction material for building structure and road infrastructures. Ensuring the durability, improving mechanical strengths, and maintaining the aesthetical values of building construction requires a search for modern and innovative materials (Pietrzak, Adamus et al. 2016). In concrete industry, the newly innovated materials are used to modernize and more functionalize the Conventional Concrete Materials (CCMs). The CCMs have brittle behavior, low strength, large water and chloride permeability, and short service life (Ma, Li et al. 2015). To fulfill the demands of construction industry, modification of concrete materials is critical.

Concrete is a mixture of cement, fine aggregate (sand), coarse aggregate, water and admixtures. But, cement is a main ingredient and acts as a binding material in concrete structures. Engineering the concrete properties to improve building structures performance and serviceability through nanotechnology and application of nanomaterial is important. Moreover, emerging smart, efficient and sustainable construction materials with improved durability and mechanical strength that can reduce the costs of maintenances and repairs is very necessary.

Concrete materials are generally intended to have long life-spans and be resistant to aggressive environmental conditions like chemical attack (like acid and sulfate), water and chloride permeability, and alkali-silica reaction. (Xu, Xie et al. 2018). However, concrete mixtures with Portland cement alone present structural problems such as cracking caused by plastic or hydraulic retraction and drying, which can make its use unviable (Pereira, de Oliveira Junior et al. 2017).

The characteristic properties of Nano Scaled Materials (NSM) are the ability to fill the voids and pores in concrete microstructure. The filling effects of nanomaterial are used to produce denser materials and therefore, the quality of bond strength & integrity between cement paste and aggregate becomes increased. Nanomaterials can be used as a means to inhibit crack initiation and growth at very early times, and prevent crack propagation in concrete structure. As a result, it is possible to produce much stronger and tougher concretes. The involvement of nanomaterials can modify concrete mechanical and durability properties through providing high specific surface area, leading to acceleration of the hydration rate and filling of the pores in CCMs (Wu, Shi et al. 2016).

The incorporation of nanomaterial could rapidly generate additional Calcium Silicate Hydrate (C–S–H) gels and hence, improves microstructure and properties of concrete material. To govern the durability, compact microstructure and optimized composition of concrete, C-S-H gels is the key issue (Wu, Shi et al. 2016). Nanomaterials have great role in concrete structure as smart nano-filler for a broad range of multifunctional composites and minimize the pore structure by reducing harmful pores to harmless pores (Chen, Ding et al. 2013).

The incorporation of TiO_2 nanoparticles into concrete caused a reduction in the air pollution concentration of nearly 20 % (Pietrzak, Adamus et al. 2016). Because of photo catalytic properties of TiO_2 nanoparticles, it is increasingly used for the production of self-disinfecting materials, self-cleaning surfaces and purifying the air from the odors (Pietrzak, Adamus et al. 2016).

The other vital material, which will be incorporated into concrete mix that intended largely to improve the splitting tensile strength, ductility and toughness, is waste plastic fiber. It is incorporated to concrete structure in order to stop or at least limit the propagation of cracks (Foti 2011). The partial replacement of sand with waste plastic fiber is not only intended to improve the split tensile strength, flexural strength, hardness and ductility, but also clearly to improve resistance against impact and fracture (Pereira, de Oliveira Junior et al. 2017). Nevertheless, the addition of fibers from tire rubber waste, polystyrene and coconut fiber in concrete and mortars diminished their compressive strength and conveying negative aspects to the quality of the ecological mixtures. But, the use of fibers from Polyethylene Terephthalate (PET) bottles is promising when compared to other solid plastic wastes (Pereira, de Oliveira Junior et al. 2017) due to its best capability to improve the mechanical strength and crack-resistant behavior.

This thesis work is aimed to enhance the crack-resistant behavior by partially substituting Cement with TiO_2 Nanoparticles (TNP) and Sand (fine aggregates) with Waste Plastic Fiber (WPF). The combined effects of these two promising materials, TNP and WPF have good properties to fill the voids or pores in CCMs, and therefore, improve the mechanical strength and physical properties, like durability through enhancing impermeability of water and other chemicals, that destroy stability of concrete structures.

The incorporation of TNP and, WPF, in this essence, waste PET bottles is believed to improve the genetic defects of cement based materials including high brittleness, and internal cracks, which lead to a decline in performance and service life of building materials and road infrastructures. The substitution of fibers mostly intended to arrest the cracks by forming bridges across micro and macro cracking in concrete structures.

Improving compressive strength, split tensile strength and water impermeability properties can be enhanced through combined effects of TiO_2 nanoparticles and waste plastic fibers and it is a strategy for long term serviceability of concrete structures. Evaluations of mechanical strength, durability properties, and characterizations of microstructure (morphology) of unmodified and modified concrete will be analyzed by complementary characterization techniques.

1.2. Statement of the problems

The CCMs have reduced resistance to cracks formations and growth. The concrete materials with Portland cement alone have low compressive and split tensile strength, high water permeability, low ductility and toughness, reduced integrity and bond strength between various ingredients in the concrete materials needs to be improved. CCMs are easily susceptible to cracks initiation and propagation through its structure. The existence of cracks in concrete structure allow water or other chemicals and materials to ingress into its structure, leading to structural and durability problems. Therefore, it requires modification through promising materials.

Introducing additional materials from millimeter scales to nanometer scales has been realized in recent years. However, the material in nano scale size has dramatic improvement ability than conventional size materials in the same chemical composition. When the mechanical and physical properties of concrete materials are improved; the ingress of chemicals and other materials will be inhibited, cracks-resistant behavior enhanced, the life expectance of concrete structures becomes increased and, hence, costs related to maintenances and repairs will be reduced.

Because of the rapid development and modernizations of the construction industry, high performance concrete (HPC) materials are in an urgent demand in entire world (Han, Wang et al. 2017). However, without developing strength, enhancing cracks-resistance characteristics and reliability of concrete materials, building high-rise structures, bridges and heavy-load structures might cause life loss and unsafe constructions. The concrete structures with enhanced performances and uniformity requisites wouldn't be achieved by utilizing conventional materials and usual mixing practices (Harilal, Rathish et al. 2019).

Meanwhile, concrete structures are generally enclosed with cracks or micro-cracks (Lang, Zhu et al. 2019) under highly confined stress caused by various mechanical, physical, and chemical processes such as external loading, shrinkage, temperature gradients, and expansive reactions. Therefore, it is very imperative to develop techniques to arrest cracks initiation and propagation from being further damaged (Lang, Zhu et al. 2019). More importantly, nano materials are required to improve concrete's mechanical and durability properties by providing high specific surface area, leading to the acceleration of the hydration rate, and filling of pores in CCMs (Ceran, Şimşek et al. 2019).

On the other hand, the substitution of sand with WPF is intended to reduce the consumption of river sand for concrete productions. Plastics materials are composed of good properties, like high durability and chemical resistance, which reinforces its popularity as building materials. Through plastics production, incineration of waste plastics are responsible for approximately 400 metric ton of CO_2 emissions per year (Tuladhar and Yin 2019). In addition, plastic materials are non-decomposable, and can cause serious harm to the environment in disturbing the balance of the ecosystem. Therefore, to minimize the adverse effects of such waste materials on the environment, it is reasonable and logical to recycle such materials through construction industry.

Plastic fibers are used to develop cracks-resistant behavior by forming bridges across micro and macro-cracking in concrete structures and, they can reduce the amount of stress concentration at the cracks tip. They are used to restraining and delaying cracks growth rate as well as redirecting its pathway and hence, improve the strength and post-cracking behavior of concrete. As to the authors (García Calvo, Pérez et al. 2019), the incorporation of waste plastic fiber is intended to prevent the development of cracks at the macroscopic scale, thus improving the long-term serviceability and mitigating the aging effects on the concrete structures.

This research thesis work is intended to upgrade concrete material properties through combined effects of promising materials, like TiO_2 nanoparticles and waste plastic fibers, to modernize the concrete technology and ensure the sustainability of the construction industry.

1.3. Objectives of the Study

1.3.1. General Objective

The general objective of this research thesis is to enhance the crack-resistant behavior of CCMs, through the partial substitution of Cement with TiO_2 Nanoparticles, and Sand with Waste Plastics Fibers.

1.3.2. Specific Objectives

The specific objectives of this thesis are:-

- Improvement of the compressive and splitting tensile strength and water permeability resistance of concrete materials by incorporating cement and sand with TNP and WPF, respectively.
- Adjusting the compositions of concrete with TNP as a partial replacement of cement to avoid reduced compressive and splitting tensile strength and improves water permeability resistance.
- Modification and morphological study of concrete materials to assure the enhancement of concrete with nanomaterials and fiber incorporations.
- Analyzing C-S-H gel formation, and identification of different compounds existing in concrete materials.
- Investigating the formation of the cracks both in TNP and fiber modified concrete, and CCMs.

1.4. Significances of the study

This research thesis is intended to contribute the following major benefits to the development of construction industry.

1. Developing crack resistant behavior through improving mechanical strength and durability properties of CCMs.
2. Increasing service life of construction building and road infrastructure that could reduce maintenance and repair cost of CCMs.
3. Developing integrity and strength between cement paste and aggregates in cement based materials, concrete.
4. Developing sustainable, smart, efficient and strong concrete materials.
5. Investigation of the combined effects of TiO_2 nanoparticles and WPF in CCMs.

1.5. Scope of the study

The main scope of this study is to conduct an experimental investigation to modify the concrete properties through the incorporation of TiO_2 Nanoparticles and Waste Plastic Fibers to cement mix in a proportion of C - 25 grade concretes, and investigating modifications in the mechanical strengths and durability properties of concrete materials.

In order to study the microstructures of concrete, the morphological study will be conducted with the help of complementary characterization techniques such as SEM, XRD & DSC-TGA.

1.6. Organization of the Study

A brief outline of the whole research thesis is presented in the following. This research thesis is categorized into six chapters. The first chapter discusses the introduction, background, statements of the problems, objectives, significance, and scope of the study. In Chapter II, various literature has been reviewed with different sub-topics. For instance, characteristics behavior of conventional concrete materials, WPF in concrete technology, and recycling of waste plastics materials in concrete technology are discussed. Moreover, concrete cracking, types, and advantages of plastics, cement hydration reactions and contributions of nanomaterial, photocatalytic activity of TiO_2 nanoparticles, and Green Concrete and CO_2 emissions from the cement industry are also highlighted. Chapter III concerns about the Materials used, a methodology of the study; and sample preparations procedure of concrete. Chapter IV, which is the core part of the thesis work, is mainly devoted to experimental parts. Mix design of concrete, concrete specimens produced, and different characterization techniques applied will be discussed in detail. Analysis and interpretations of the experimental results, and discussions are discussed in chapter V. The thesis is completed with a short chapter presenting the main conclusion of this thesis work.

Chapter Two: Literature Review

2.1. Characteristics Behaviors of Conventional Concrete Materials

Nowadays, because of the increase in population and urbanization, it is necessary and highly demanded to provide safe concrete structures, and concrete materials (Feng, Su et al. 2019). As the population increase, the demands of land to the housing and changing local area to urbanization become increased. Therefore, availability of land to the increased population, and accommodating large numbers of population for housing is difficult. This requires building of high rise structures with improved strength, and stiffness in small space. But now, consuming the traditional concrete materials and building of long and large structures is common in developing countries. The characteristic behavior of CCMs is that it could easily form cracks under high local stress that caused by various mechanical, physical and chemical processes such as external loading, shrinkage, temperature gradients, and expansive reactions.

Cracks provide pathways to hostile species such as water, chloride and sulfate ions which, leads to concrete structure deterioration and steel reinforcement corrosion, which might result in strength and stiffness loss of concrete structures, and even failures (Feng, Su et al. 2019). Cracks reduce the mechanical performance of the concrete structure and thus, limits its durability (García Calvo, Pérez et al. 2019).

CCMs characterized as extremely quasi-brittle failure and have low split tensile strength; which makes it susceptible to the propagation of uncontrolled cracks (A and M 2017). These serious shortcomings of concrete properties impose constraints in structural design and affect the durability of concrete structures. To overcome these disadvantages of CCMs, it is a promised method to incorporate nanoparticles into the concrete structures to prevent sudden failure and to prolong the service life of concrete structures (Chen, Ding et al. 2013).

Nowadays, research works are emphasized on benefits of nanomaterial and nanotechnology in various fields such as medicine, automobile industry, construction, energy, telecommunication and informatics. This is due to the special characteristics of nanomaterials to enhance the durability properties and to reduce environmental pollution by reducing the carbon footprint of the buildings. The addition of nanomaterial into concrete mix helps to control the degradation of the calcium silicate hydrate reaction that caused by calcium leaching in water, block water penetration, and leads to improvements in durability.

The incorporation of nanoparticles into concrete mix, is gaining an attention due to their high surface area and therefore, high reactivity to improve the mechanical properties of C-S-H gel, reduce porosity and modify the durability of cement matrix (Jalal, Mansouri et al. 2012). The C-S-H gel, is responsible for the physical and mechanical properties of cement-based materials, including creep, shrinkage, permeability, porosity and elasticity of concrete.

As recent investigation shows, nanoparticles with a very insignificant dosages will changes the hydration kinetics of entire cementitious system and result improvement of compressive strength, flexural strength, microstructure, pore size and distribution and, are the most widely used materials today. Therefore, the limitation in CCMs requires findings of promised materials to improve its properties.

2.2. WPF in Concrete Technology

The partial replacement of sand with WPF was targeted to enhance the crack resistant behavior of concrete structures by improving the split tensile strength, ductility, toughness, and make the environment free from air pollution and also, reduce soil acidification. Fibers are highlighted as promised material to solve the problems of cracking (Pereira, de Oliveira Junior et al. 2017), in addition to the improvement of the structural aggregation between concrete components.

For sustainable infrastructure systems, higher durability and to have a long maintenance free performance with low repair costs, and therefore, scientists and engineers have greatly engaged. In other words, enhancing built infrastructure service life will lessen the demand for new infrastructure, resulting in little raw materials usage, less energy consumption, and reduce CO_2 emissions.

Concrete structures usually contains cracks or micro-cracks in dynamic loading, such as impacts, blasts, earthquakes, and these cracks may easily initiates and propagates; and finally weaken the concrete strength, and structure instability (Lang, Zhu et al. 2019). The utilization of WPFs in the production of concrete has revealed possibility towards ductility, toughness, impacts and fracture resistance of concrete. The application of WPF into concrete composition helps to assure the sustainability and green construction.

As the (Alani, Bunnori et al. 2019) investigations showed, the inclusion of recycled PET fibers as concrete reinforcement materials apparently achieves excellent performance in terms of tensile, crack resistance and ductility of concrete structures.

The partial replacement of sand with grinded PET bottles can improve the durability properties (porosity, permeability, and water absorption and chloride penetration) of concrete. For instance, adding grinded PET bottles have improved the chloride permeability of concrete. Furthermore, waste PET fiber as a replacement material with sand has lowered water absorption and concrete material porosity (Alani, Bunnori et al. 2019).

The incorporation of WPFs could have significant effects on development of strength, and impact resistance of concrete composites (Mustafa, Hanafi et al. 2019). CCMs most serious drawback is its very low splitting tensile strength. Because of this limitation, cracks develop and propagate in concrete structures, which can lead to a reduction in their durability or to their failure. In addition to that, involving waste materials in the concrete composition is one of the ultimate strategies to manage it. Currently, in two directions research conducted on fibers in concrete technology: one aimed at developing greatly to increase the load-bearing capacity of concrete structures and the second is aimed at environmental benefits from recycling (Grzymski et al.2019).

2.3. Recycling Waste PET bottles in Concrete Technology

Plastic production has begun, since 1950s, and the rate of production and its use increased rapidly. Annually, plastics production increased from 2Mt in 1950 to 335Mt in 2017, in worldwide (Tuladhar and Yin 2019). This is due to the changes in living styles and consumption of plastics products in the entire world. The PET plastics products and amounts increased from time to time due to increased demands of mineral drinking water, juice, oil and other similar liquids.

In Ethiopia context, there are many company engaged in PET bottles production; private limited and government led company with different sizes, shapes and thickness. For example, Aqua Plastic PLC, private led Company produces 200,000 PET bottles per day and Addis Ababa bottles and glasses manufacturing SC, established in 1976, the largest PET bottles supplier have 81 million bottles production in 2016, but now have 250 million PET bottles production per year.

Most of these plastics, especially packaging plastics, are single used products and are discarded after short first uses, and only 9 % to date have been recycled, so far (Tuladhar and Yin 2019). However, recycling rate of paper & steel are 58 % & steel 70 – 90 %, respectively.

Researchers have found that the waste plastic material can persist on earth for about 4,500 years without degradation. Majority of the waste plastic ends up in landfills & in the nature causing serious environmental influences. It is estimated that 5 to 13 Mt of non-biodegradable plastic waste every year into oceans, causing serious adverse effects on marine environment. The more ecological & desired alternatives for plastic industry is a "circular economy" approach, where emphasis is given to repairing/reusing products during their service life (Tuladhar and Yin 2019)

Numerous studies have proven that the health hazard caused by the inappropriate disposal of plastic waste, for example reproductive problems in human and animal, genital abnormalities etc. Recycling of plastic wastes in concrete industry is better option to reduce emission than incineration of it. In the modern economy, plastics materials widely used in almost every sector due to their light weight, low cost, durability, & versatility.

2.4. Types and Advantages of Plastics

There are various plastics types that are listed and described in table 2.1. These all plastics products are classified into one of the three plastic categories. These are thermosets plastics, which continue in a permanent state once it is hardened. Due to this, it can resist high temperature without losing shape. The second one is elastomer plastics, which cannot melt and turn into a gaseous state. The third one is thermoplastic plastics, which can be re-melted and can change its shape on heating.

Table 2.1: Various plastic types and their advantages

Name of plastics	Advantages	Disadvantages
Polyethylene terephthalate (PET)	▪ Packaging of soft drink, water bottles, detergent and cleaning containers, peanut butter and other food containers. ▪ PET products are possibly reprocessed into new bottles and also most easily recyclable in construction industry as coarse or fine aggregates. ▪ Used to improve concrete plasticity and delays micro cracking. Moreover, their presence limits the width of the cracks in concrete (Grzymski et al. 2019). ▪ The PET fibers increased the ductility of concrete (Foti 2011).	Non decomposable and negative impacts in the air, in the water and on the land
High Density Polyethylene(HDPE))	▪ For milk and water jugs, laundry detergents, motor oil containers, and shampoo bottles are easily recycled into new containers. ▪ It is used to engage the concrete matrix post-cracking phase in the work and reduce the shrinkage effects (Grzymski et al. 2019).	Non decomposable and negative impacts in the air, in the water and on the land
Polyvinyl Chloride (PVC)	▪ Window cleaner bottles, plastics squeeze bottles, cooking oil and peanut butter jars, vinyl pipes and window and door frames.	Harmful constituents created by its dumping
Low Density Polyethylene (LDPE)	▪ For bread frozen food, and grocery bags and most plastics wraps.	Not usually recycled

Polypropylene (PP)	▪ for syrup, yogurt and margarine containers, disposable diapers, baby bottles ▪ Used to improve mechanical strength of concrete whether they are new or recycled (Grzymski et al. 2019).	Not easily recyclable
Polystyrene (PS)	▪ For rigid polystyrene CD cases, food containers, egg cartons, building insulation.	Recyclable, but not economical

2.5. Nano-materials in Concrete Technology

The partial replacement of nanomaterials in concrete technology could rapidly generate C–S–H gel (Sobolev 2016) and hence, improves the strength and durability properties of the concrete. Nanomaterials modify the microstructure of concrete technology. It contributes, its role as nano-filler and minimizes the pore structure by reducing harmful pores (Ma, Li et al. 2015). The amorphous phase, C–S–H is the "glue" that holds concrete ingredients together and, is itself a nanomaterial (Sobolev 2016).

Concretes that contain nanomaterial in its structure has reduced pore size and distribution, more dense structure than CCMs, and hence, improved compressive and splitting tensile strength, flexural strength (Paul, van Rooyen et al. 2018). Nanomaterials are highly demanded to enhance durability of concrete structures; by reducing the penetration of water, chlorides, acids, sulfates and alkali-silica reactions. Nano-materials intended to fill the voids or pores inside concrete, and also improved the interface structure of concrete and aggregate to increase the strength, toughness, impermeability and durability of concrete (Ma, Li et al. 2015). Partial replacement of nanoparticles into concrete structure is essential to develop the crack-resistant behavior of concrete.

Therefore, it is very imperative to develop techniques that help to arrest the cracks initiation and propagation (Lang, Zhu et al. 2019) in concrete structure. Several properties of concrete can be adjusted by means of chemical additives during the initial steps of production and help to achieve improved hardness, modified density and reduced rate of curing (Mora, González et al.

2019). The durability of concrete becomes improved, the maintenances and repair cost becomes reduced.

2.6. Reactions of Cements and Contribution of nanomaterials

The chemical reaction of cement and water undergoes is known as hydration reactions. A cement particle is composed of four chemical compounds namely, tricalcium silicate (C_3S) or alite, dicalcium silicate (C_2S) or belite, tricalcium aluminate (C_3A), and tetra calcium alumino-ferrite (C_4AF). Hydrations of the C_3S or C_2S with water lead to the formation of C-S-H gel and calcium hydroxide (CH). The C-S-H gel is a tough bond and forms strong assembly between the concrete particles. However, Portlandite is a resolvable product and leaches-out in water.

The physical properties of C–S–H are to control the setting time and hydration reaction of cement. Moreover, the setting time and the early strength development of cement are attributed to the hydration of alite, which is utmost abundant and vital cement mineral in Portland cement, whereas the long term strength increase (approximately 1 year) is associated to the hydration of belite. Effectively; strength development, shrinkage and durability of the hardened cement paste is highly depends on the C–S–H gel formation (Paul, van Rooyen et al. 2018). During the first few days, much of the reaction occurs, that leading to significant strength gains and reduction in capillary porosity.

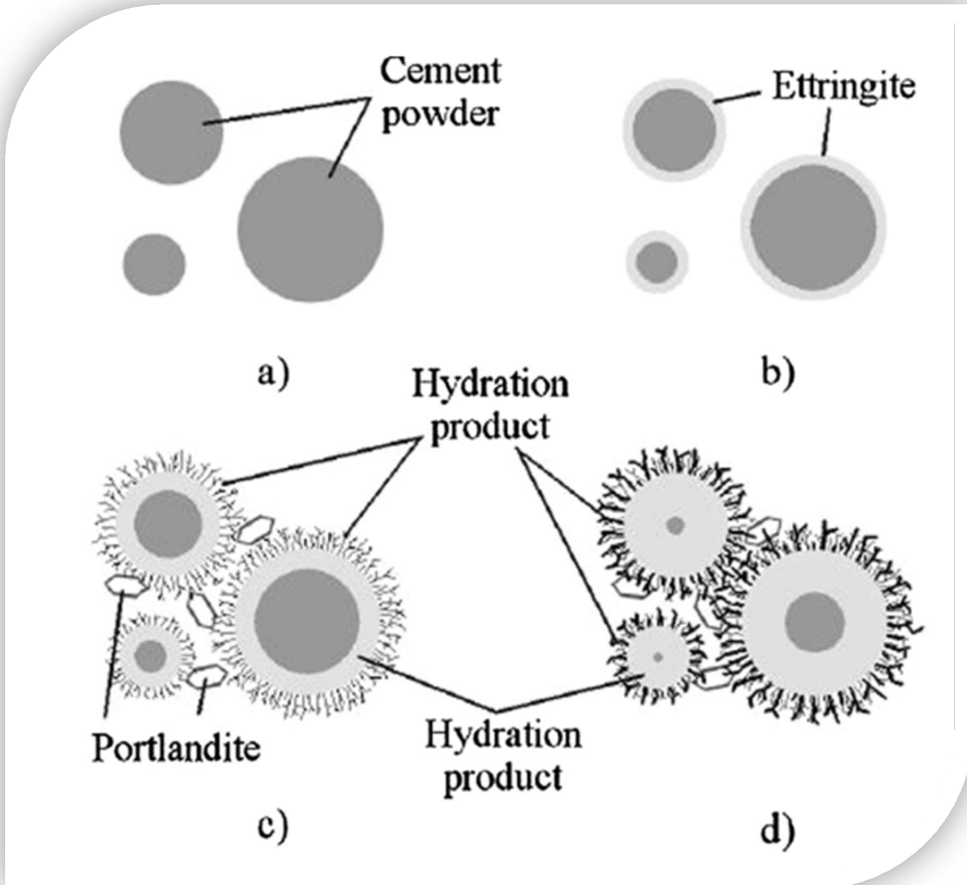


Figure 2.1: Stages of cement hydration process (Paul, van Rooyen et al. 2018)

As result of addition of water in Figure 2.1a, a film is formed on the surfaces of cement particles (see Fig. 2.1b). After some time, this film is saturated with water and forms C–S–H gel and the Portlandite as shown in Fig. 2.1c. The hydration still continues but at a lower speed, because the C–S–H gel hinders the diffusion of water toward the nucleus of the cement powder, which can remain unhydrated for years (see Fig. 2.1d). The chemical formulas, expressing the hydration of alite and belite can only be approximated as shown in Equations (1) and (2) below.

$$C_3S + (1.3 + x)\,H \text{ -----------> } C_{1.7}SHx + 1.3CH \text{ ------------- } 1$$

$$C_2S + (0.3 + x)\,H \text{ ------------> } C_{1.7}SHx + 0.3CH \text{ -------------} 2$$

Where C1.7SHx is the calcium silicate hydrate (C–S–H) gel phase and CH is calcium hydroxide, which has the mineral name portlandite. x - represents the amount of water associated with the C–S–H gel, which varies from about 1.4 to 4 depending on the relative humidity inside the paste and on how much of the water associated with the C–S–H is considered to be part of its actual composition. C–S–H is a semi-amorphous gel-like material that comprises approximately 70 wt. % of the hydrated cement composition and is the main binding material. $Ca(OH)_2$ (s) is crystalline and comprises roughly 15–20 % of the hydrated cement.

Apart from C–S–H, the second main hydration product is CH or Portlandite. This is mainly formed from alite hydration. It has a Ca/Si ratio of about 3:1 and C–S–H has a Ca/Si ratio of approximately 2:1, so excess lime is available to produce CH. Therefore, monitoring of the portlandite level is significant as it can yield information on the reactivity of cement. Nanotechnology contributes in meeting the huge demand for infrastructure in a sustainable manner (Saloma, Nasution et al. 2015).

Nanomaterial was first announced by famous lecture of Nobel Laureate Richard P. Feynman "There is Plenty of Room at the Bottom" given in 1959 at the California Institute of Technology (Mo and Howser 2013). A clear definition of nanotechnology was set in 1981 by Drexler (Drexler1981), in that materials are produced in a dimensions and precision of between 0.1 nm and 100 nm. In medium terms, nanotechnology involves the study at microscopic scale ($1 \text{ nm} = 1 \times 10^{-9}$ m) (Gajanan and Tijare 2018).

Nanotechnology is being adopted to improve the performance of construction materials like concrete. The main characteristic of nanoparticles is that they have high surface-area-to volume ratio (Paul, van Rooyen et al. 2018). Therefore, more atoms can be expected on the surface of nanoparticles rendering them highly reactive. For a clear understanding and engineering of complex structure of concrete, incorporation of nano-scale materials will definitely result in a new generation of concrete, which is stronger and more durable, with desired stress resistant behavior and, introduced "smart" properties.

As the surface area of a material increases, there is great opportunity for large amount of the material can come into contact with the surrounding materials and therefore, to affect the reactivity. Nanotechnology mainly considers the benefits of size to control material properties, as you reduce the materials size to nano scale that can change abruptly the materials properties.

The progresses in nanotechnology have a great impact on the field of cement based materials, like concrete & mortars. The nanotechnology can facilitate the development of nanomaterials that will incorporate into concrete materials to increase their mechanical strength, and decrease environmental impacts. Synthesizing and engineering of a new material with new properties are required to enhance concrete properties for the modern concrete structures. The same material at the nano-scale can have properties (e.g. optical, mechanical, durability and electrical), which are very different from, and even opposite to the properties that the material has at the macro-scale (bulk).

The durability of concrete is principally dependent on the capacity of a fluid to enter into the concrete's microstructure, which was called permeability (Zhang and Zong 2014). High permeability of concrete directed to the introduction of molecules that react and destroy its chemical stability. Low permeability of concrete highly help to resist the penetration of water, sulfate ions, chloride ions (Peng, Hu et al. 2019), alkali ions, and other harmful substances which cause chemical attack. Permeability of Concrete had a close association with the characteristics of its pore size and the concentration of micro-cracks at the aggregate to cement paste interface as well as within the paste itself (Zhang and Zong 2014).

2.7. Metal Oxide Nanoparticles (MONPs) in Concrete

The metal oxides nanoparticles reacts with $Ca(OH)_2$ or (CH) and, then increases the number of C-S-H gel, which used to make more compacted microstructure and, thereby decreases the permeability, and improves the mechanical properties such as flexure, compressive strengths and abrasion resistance (A and M 2017) of concrete.

The main advantages of incorporating MONPs in the construction industry are its capability and good mechanical properties. MONPs have the following advantages in concrete industry.

- It gives high strength in concrete for the particular applications.

- It will helps to reduce some quantity of cement in concrete without compromising strength and therefore, creating positive environmental impact on construction materials.
- Nano materials will raise the strength in concrete within a short curing time and lessens the construction time period.
- The addition of some of the metal oxides present in the nano particles into concrete, can reduces the permeability of concrete. Because of this feature the concrete will strengthen and, there after we can advance the durability characteristics.
- The nanoparticles acts as filler and increases the density by filling the micro-voids between cement grains.
- The well-dispersed nanoparticles used as crystallization promoter in order generate cement hydrates, therefore accelerating the hydration process.

According to the different investigators, there are three different effects of TNP on cement hydration (i) site effect; the TNP provides additional sites that promote heterogeneous nucleation, (ii) dilution effect; the addition of inert TNP reduces the percentage of reactive cement, and (iii) filler effect; the TNP tend to fill the voids between larger particles, and reduce the inter-particles distance, thus increasing the packing density. Some very important MONPs are explained hereby.

2.7.1. Titanium Dioxide Nano-particles, TNPs

TNPs are very small particles that accelerate the early age hydration of Ordinary Portland Cement (OPC), increased the compressive strength, flexural strengths, and abrasion resistance of concrete structures. The increase in compressive strength was due to promoted cement hydration and by acting as nucleuses for cement pastes and thus, densifies microstructure and interferential transition zone, fill pores and reduced porosity found in CCMs.

TNPs are added to concrete material to improve its properties. It used to break down organic pollutants, and bacterial membranes through powerful photo catalytic reactions, and therefore, helps to reduce air pollutants when it’s applied to outdoor surfaces. Its hydrophilic character gives self-cleaning properties to concrete building surfaces. Therefore, the resulting concrete surface will not lose its white color.

2.7.2. Some Other Nanoparticles in Concrete Industry

Nano Al_2O_3, partial replacement of cement leads to the calcium-aluminum-silicate (C-A –S) gel formation in concrete. It helps to improve mechanical properties such as compressive and tensile strength of the concrete. It has also ability to decrease the water absorption and chloride penetration, and then, enhance the durability of concrete materials.

Nano-silica particles, leads significantly to reduce the amount of cement needed. This will have significant impact on the environment by reducing the damage induced by CO_2 emissions.

Nano-clay particles, used to enhance mechanical performance, resistance to chloride penetration, self-compacting properties and reduce permeability and shrinkage of concrete. It is well known that, ingress of chlorides into concrete initiate corrosion of steel reinforcement and deteriorates concrete member and affecting the durability of reinforced concrete.

Carbon Nanotubes/Carbon Nano fibers, used as the nano reinforcement in cement based materials. It will give the greater strength in terms of modulus of elasticity (TPA) and the tensile strength (GPA) and it has distinctive chemical and electronic properties (A and M 2017). Nano materials can strengthen the mechanical properties of the cement based materials, like concrete. In the present days carbon nanotubes and carbon nano fibers were the most extensively used research materials for development of construction industry.

The properly incorporated CNTs into concrete mix will have remarkable applications in the concrete structures. It can fill voids in conventional type of concrete. Because of the voids in concrete materials, water and other deleterious chemicals can penetrate and will cause concrete cracking. Therefore, the filling of voids in conventional concrete with nanoparticles of metal oxide and CNTs/CNFs can reduce the concrete cracking. CNTs and CNFs gives the greater strength with high modulus of elasticity is represented in terms of TPA and the tensile strength represented in the order of GPA.

CNTs/CNFs are facing a major challenge in the availability, with high purity, uniformly dispersed and also, the cost aspects. There are no available methods that can produce enormous amount of CNTs with cleanness and quality in terms of kilogram amounts. CNTs/CNFs have high price and so, it is difficult for commercial applications. But, the present scenario shows in the last 2-3 years (A and M 2017), changes in developing these products.

Several companies came forward to start and manufacture the CNTs. The problems of availability and cost will be solved in the coming few years in construction sector. The other main challenge in the CNTs/CNFs was proper dispersion that will be take place in the cement paste, partially due to their hydrophobicity and strong self-attraction between CNTs/CNFs in the cement composites.

2.8. Concrete Cracking

Institute of American Concrete, in its Guide for Making a Condition Survey of Concrete in Service, that published in the 1968 ACI Journal, has defined cracks as an incomplete separation of materials into one or more parts with or without space between them. Cracking of concrete is a common complaint and initiated by restraint (internal or external) of volume change, commonly brought about by a combination of factors such as drying shrinkage, thermal shrinkage, curling, settlement of the soil support system, and applied loads. Cracking can be significantly reduced, when the causes are understood and preventive measures have been taken. The following figure shows cracked surface of concrete.

Figure 2.3: Cracking of concrete (Eng. Sdeiq Jalal Abdullah, 2013)

Concrete is a brittle material and, cracks will occur due to its inability to be flex under high and moderate stress. Cracks can easily spread through CCMs, because there are no fibers to hold the surrounding substances together. In order to prevent cracking of concrete, incorporation of very tinny or nanomaterial and fibrous substance is very imperative. Concrete in its plastic state, which lasts from casting to about 3–8 hrs, undergoes changes that strongly influences the properties of the hardened material (Kayondo, Combrinck et al. 2019).

The challenge with cracks is that they become pathways for deleterious elements into the deeper zones of the concrete, and hence, leading to reinforcement corrosion. Figure 2.4 shows how water and alkalis diffuse into the concrete structures and cracks will be formed.

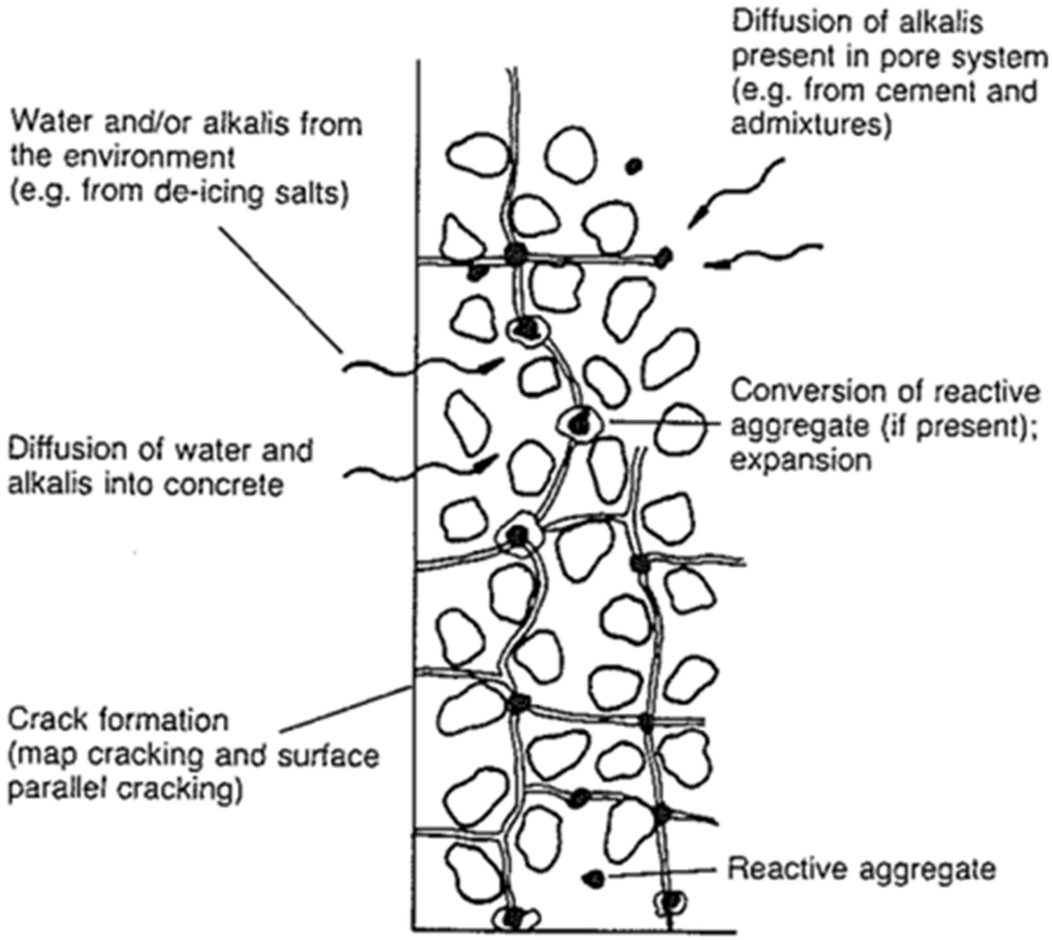


Figure 2.4: Water and alkalis diffusion and cracks formations (Thomas Telford, 1992)

Cracks in the concrete structure reduce the load carrying capacities and are also preferential ways for ingress of aggressive agents, and thus even encouraging the reinforcement corrosion. Since, repairing the damage is usually difficult and expensive, exhaustive studies are being done to control the formation of cracks in concrete structure. Fibers bear additional loads through bridging action after the appearance of first crack and via decreasing the amount of stress concentration at the tip of crack, restraining and delaying its growth rate as well as redirecting its path, improve the strength and post cracking behavior. Fibers are more effective in the post-cracking, and preventing the spread of cracks.

Concrete structures subjected to tensile stresses crack due to the brittleness of the concrete materials. The concrete brittleness behavior can be reduced by addition of fibers (Grzymski et al. 2019). The leading function of the fibers is to bridge cracks appearing in the internal structure of the concrete and to enable the concrete elements to deform plastically. The existence of fibers contributes to the reduction of stress concentration at the cracks end, which, if the fibers where absent, would accelerate the propagation of the cracks. A schematic stress distribution within a crack with and without fibers is shown in fig 2.5. In the initial stages of cracking, the fibers slow down the development of micro-cracks in the concrete structure and have much greater energy absorbing capacity than unincorporated concrete.

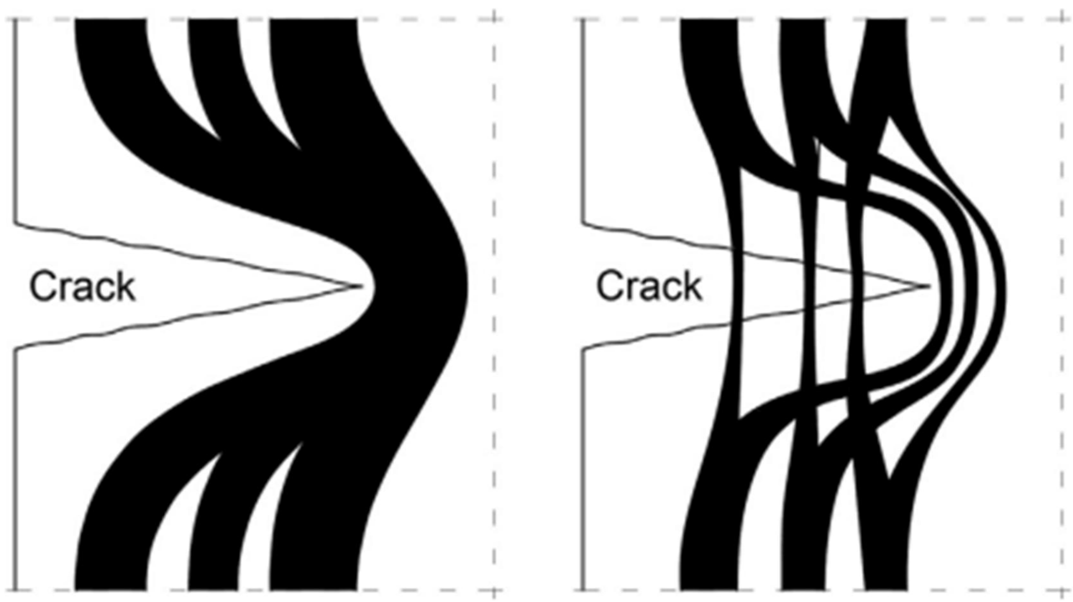


Figure 2.5: Concrete cracking without (left) and with fibers (right), (Grzymski et al. 2019)

2.9. Durability of Concrete

It is defined as the ability of a material to resist weathering action, chemical attack, abrasion and other conditions (Abed and Nemes 2019). The durability properties of concrete materials generally depend on permeability of water, migration of chlorides, and water absorption. It also depends on the properties of concrete ingredients, their mixing method and proportions. Water penetration is the flow of water through pores in concrete.

An application of nanotechnology in construction industry is an effective way to improve durability properties and, also reduce environmental pollution (Saloma, Nasution et al. 2015). An innovation in material technology is needed to obtain higher performance concrete. The measures of high-performance concrete are the workability, uniformity, strength, durability, and stability. Durable concrete is the one with ability to last a long time without significant deterioration.

A durable material has great contribution in conserving natural resources, reducing wastes and costs of repair and replacement. The production for replacement of building materials depletes natural resources and generates air and water pollution. The design service life of most buildings is 30 years, although some buildings often last 50 to 100 years or longer.

Nanomaterials have the possibility to modernize the construction industry by successfully improving the performance and durability of construction materials, as well as imparting new functionalities to these materials.

2.10. Factors affecting the durability of concrete

Concrete structures are commonly subjected to aggressive environmental conditions from a variety of naturally-occurring and industrial chemicals.

2.10.1. Sulfate Effects

The effect of sulfate is one of the most significant factors in the deterioration of concrete structures. The effects produced by sulfate are referred to the products formed from the reaction of sulfate ions and the calcium aluminate hydrate and calcium hydroxide, present in the cement.

These products are ettringite and gypsum, which cause expansions and cracks in the concrete, which subsequently causes the surface to become weak & reducing durability. The reduction in durability of concrete is not only because of the expansion effect of sulfate, but the sulfate also causes a reduction in the adhesion forces of the structure by injuring the critical phases of hydrate Portland cement, i.e., calcium hydroxide and calcium silicate. This reduces strength and causes a reduction in concrete durability.

2.10.2. Acid attacks

The other possible risk to concrete are usually takes place due to its exposure to acid attack. Acid attacks on concrete can occur in a variety of ways. Concrete structures can be attacked by acids in groundwater or soil, either naturally occurring or due to the dumping of chemical wastes from industrial processes.

The mechanisms of acid attack differ comparing to the type of acids. Among the acids, which affect the concrete structures such as sulfuric acid (H_2SO_4), carbonic acid (H_2CO_3), hydrochloric (HCl) and nitric acids (HNO_3) are the most common acids encountered by concrete. The general effect is the dissolution of cement hydrates and calcium hydroxide, as calcium salts, which weakens the exposed concrete.

The carbonaceous aggregate (such as limestone and dolomite used in concrete production) is susceptible to acid attack. Because of attacks from sulfuric acid (H_2SO_4); both dissolution and swelling of concrete will take place. As to the results of (Diab, Elyamany et al. 2019), a loss in the weight of concrete will be occurred when exposed to sulfuric acid. Sulfuric acid can react with the calcium hydroxide and the calcium silicate hydrate gel in concrete and then, form gypsum. This phenomenon is called gypsum corrosion, which causes the dissolution and swelling of concrete.

This gypsum corrosion reduces the alkalinity of concrete, which induces microbiological corrosion. The product of corrosion is a weak compound with no cementitious properties, and eventually, leads to the early deterioration, loss of strength and, in extreme cases, the destruction and collapse of the concrete structure. To improve the performance of concrete against acid attacks is to reduce the permeability of concrete.

2.11. Cement Production and Emissions

According to (Hussein et al.2016) findings, in worldwide 4 billion metric tons of OPC produced annually. The ever-increasing demand for concrete has also increased the production and transport of cement, which alarmingly increased the energy consumption and greenhouse gas (GHG) emissions. For example, worldwide demand of OPC by the 2050 is expected to boost nearly 200%. Therefore, ensuring environmental sustainability through enhancing the concrete structure durability and elongation of service life is advisable. The increased servicing life of concrete structure can be achieved due to the development of smart and durable concrete materials.

It has also been estimated that worldwide cement production accounts for approximately 7% of the CO_2 emissions (Harilal, Rathish et al. 2019). As International Energy Agency (IEA) reports suggest, that it amounts to 6-7% of total CO_2 emissions in 2016 (Hussein et al.2016). Therefore, the alternative solution for that matter is the construction of concrete structures with higher mechanical strength and higher durability, which will decrease their maintenance requirements or need for early replacement. The mixtures of cement composites and nanomaterial can increase the mechanical strength and durability of concrete structures.

So that, the application of nanotechnology is an effective way to reduce environmental pollution and improve durability of concrete (Saloma, Nasution et al. 2015). Nowadays, there was great interest to replace the traditional ingredients of concrete components by a newly obtained material, in order to decrease particulate and gaseous emission from cement technology, & also to increase its performance & durability. Partially replacing cement with nanomaterials as one of the components is used to reduce the cement consumption & accordingly, GHG emissions. According to the investigations of (Lum, Lee et al. 2019), nano-materials have been applied in the construction sectors, aiming to increase the strength and durability, while reducing pollution at the same time.

During the production process of cement and concrete, environmental issues such as high energy consumption and emittance of CO_2 are highly undesirable phenomena. Therefore, the application of nanomaterial is used to alleviate the limitation. Various stages in cement manufacturing technology, which generates particulate and gaseous emissions represented in figure 2.5.

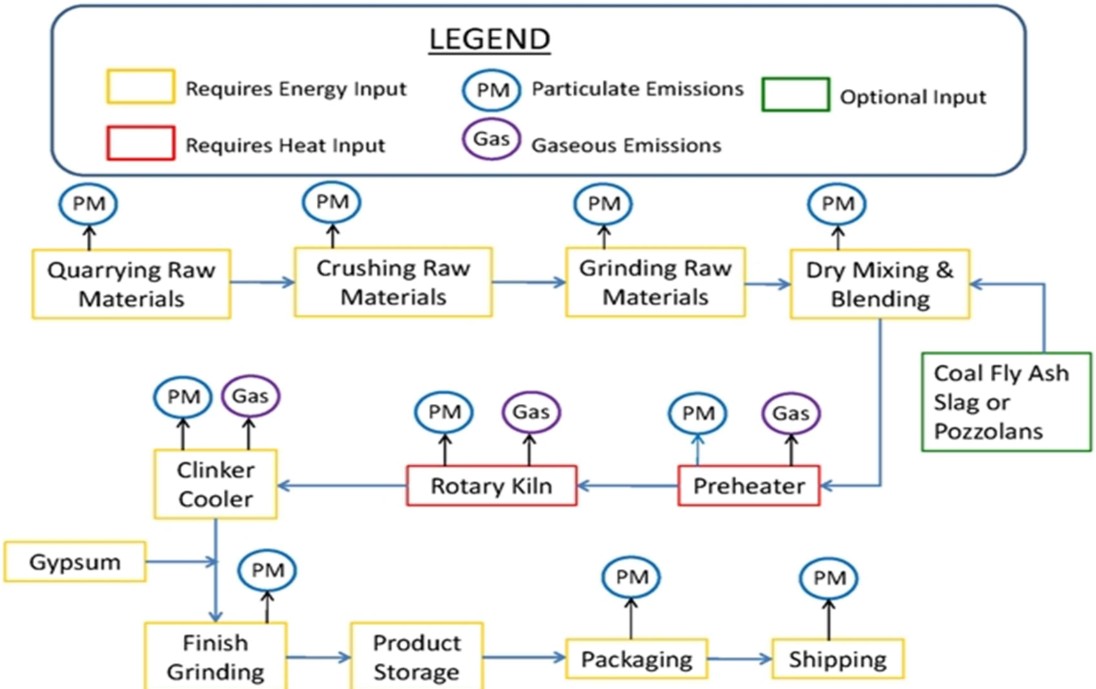


Figure 2.6: CO_2 Emissions from cement factory

In cement manufacturing, mainly there are two chemical reactions that generate CO_2 emissions. The first one is involved in the production of the main components of cement clinker, as carbonates (largely limestone, $CaCO_3$) are decomposed into oxides (largely lime, CaO) and CO_2 by the addition of heat. Only in this step, about 5 % of total anthropogenic CO_2 emissions will be generate (Robbie M. Andrew, 2018).

The second one is the combustion of fossil fuels to generate energy required to heat the raw ingredients to around 1450 ^{o}C, and these energy emission, includes electricity emissions. The total emissions generated from the cement industry could contribute as much as 8 % of global CO_2 emissions (Robbie M. Andrew, 2018).

Concrete is known man-made and widely used construction material that emits particularly, high amounts of environmentally damaging waste over its life cycle of production, construction, maintenance, and eventually demolition (Hyoung Kim et al.2016). Concrete is next to water, the most consumable material in this planet, even it contains cement, the key ingredient that composed of massive carbon footprint.

2.12. Green Concrete

Green concrete is characterized by the application of industrial by-products or alternative materials for wise utilization of natural resources and to save energy in cement industry as well as minimizing environmental pollution. The production of concrete-making materials or ingredients usually needs high energy, costs, and causes environmental pollution (Warati, Darwish et al. 2019).

The increased call for concrete production, leads to the reduction of virgin concrete elements, which is a serious issue for all stakeholders of the construction industry for sustainable economic growth. Hence, there is a need to offer more consideration to construction materials with concerns to the economy, wisely energy utilization, and environmental protection for sustainable development. Fine aggregate is one of the ingredients of concrete that needs to get considerable attention in the production of green concrete, and it usually comprises up to 30% to 35% of the total volume of concrete (Warati, Darwish et al. 2019). Natural or river sand is universally used fine aggregate in the production of concrete. Replacing these fine aggregate with WPFs, is intended to reduce the depletion of virgin aggregates and also, it is strategy to produce green concrete in Ethiopia.

Nowadays, a lack of natural or river sand has become a problem for the construction industry in Ethiopia, as a result of growing construction activities in many parts of the country, significant depletion of natural sand take place. Therefore, it is time to partially replace natural sand with locally available waste plastics material without compromise the quality of concrete.

2.13. Photo catalytic properties of TiO_2

Photo catalytic oxidation is a promising and sustainable solution for decomposition of organic compounds and removal of harmful gases (Xu, Bao et al. 2019). As air pollution becomes a pressing concern in many major cities of worldwide, concrete made with TiO_2 material shows great promise in improving air quality (Pietrzak, Adamus et al. 2016). TiO_2 nanoparticle is used as a photo-catalyst in emerging photo catalytic concrete for pollutant abatement. TiO_2 nanoparticles incorporated into concrete has high efficiency in reducing NO_x (Pietrzak, Adamus et al. 2016).

The cement added with TNP can be used to build a photo catalytic concrete with self-cleaning and air purification characteristics. The concrete with TNP incorporation can allow effective photo catalytic decomposition of pollutants (Organic compounds, carbon monoxides, chloro-phenols, and aldehydes) generated from automobiles and industrial emissions.

Photo catalytic concrete is a green material. Applying photo-catalytic concrete, building structures looking new for a decades. Inside hospitals and laboratories, the spread of germs can be minimized and urban air quality can be improved. Environmental purification and sustainable development can be contributed through developing of photo catalytic building materials. At present day, building of durable and attractive looking construction not justifies the use of concrete. One of the most important opinions to the protection of environmental is the use of ecological concrete. To reduce harmful compounds in the air surroundings the concrete buildings and removal of impurities, which accumulate on the concrete surface over time, TiO_2 nanoparticle addition is important.

TiO_2 nanoparticles incorporated concrete, after being subjected to the influence of UV rays became activated. In the later stages of the process, OH^- hydroxyl radicals with strong oxidizing properties are formed in the presence of rainwater on concrete surface. The decomposition of harmful substances in the surrounding air as well as contaminants on the concrete surfaces accelerated through the natural process of oxidation. TiO_2 nanoparticle is not consumed in the ongoing reaction processes and is long lasting and renewable. The following reactions show how the oxidations of harmful NO_X into harmless NO_3^- nitrate ions take place.

1) Oxidation of nitric oxide NO to nitrogen dioxide, NO_2

   $NO + 2OH^- \rightarrow NO_2 + H_2O$ -- (1)

2) Reduction of nitrogen dioxide to nitrate ions, NO_3^-

   $NO_2 + OH^- \rightarrow NO_3^- + H^+$-- (2)

3) Reduction of nitrogen oxides to nitrate ions, NO_3^-

   $NO_X + O_2^- \rightarrow NO_3^-$ --- (3)

Finally, nitrate ions form nitric acid on the concrete surface, and which in turn reacts with grout constituents and create neutralized salts (nitrate) and then, washed out by precipitation.

Chapter Three: Materials and Methods

3.1. Materials

3.1.1. Cement (Binder material)

Locally available Ordinary Portland Cement (OPC) 42.5 R grade; which was manufactured by Dangote cement industry has been used as a binder material. Cement is the most known binding material and produced by conforming EN 197-1 – CEM I 42.5 standards specification. It is a finely ground grey powder and chemically formed by combining raw materials containing calcium oxide (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) and other ingredients in very small percentages.

It is produced by heating this mixture to a high temperature around 1450 ^{o}C, and then grinding the resulting material (clinker), with a small quantity of calcium sulfate ($CaSO_4$) gypsum. It has been stored in dry place and away from moisture to ensure in good condition during the experimental period. There are four major mineral constituents produced inside the rotary kiln, during the mixing process of the cement ingredients. These are main compounds that participate in strength gaining process at different stages of concrete.

Tricalcium silicate (C_3S) hydrates and hardens quickly, and it is extremely responsible for initial set and the early strength gain, whereas tricalcium aluminates (C_3A) hydrates and hardens the rapidest. C_3A also releases a large amount of heat immediately and contributes slightly to the early strength. The rapid hardening nature of C_3A is the due to gypsum i.e. added in the cement production. Dicalcium silicate (C_2S) hydrates and hardens gradually, and is very much responsible for long term strength increase i.e. beyond one week's time. The least contributing component of concrete is tetra calcium alumino ferrite (C_4AF), but still it hydrates rapidly. The chemical compositions of cement information (data) incorporated below separately.

The chemical compositions of cement type CEM – I, according to the ASTM C-150 are found in the table 3.1.

Table 3.1: Chemical mineral and oxide composition of cement, CEM I

Constituents of Cement	OPC % by wt.
lime (CaO)	64.64
Silica (SiO_2)	21.28
Alumina (AlO_3)	5.6
Iron Oxide (Fe_2O_3)	3.36
Magnesia (MgO)	2.06
Sulfur Trioxide (SO_3)	2.14
N_2O	0.05
Loss of Ignition	0.64
Lime Saturation Factor	0.92
C_3S	52.82
C_2S	21.45
C_3A	9.16
C_4AF	10.2

Table 3.2: Physical properties of cement type, CEM – I

Property	Test result	Test methods
Fineness (m^2/kg)	269.5	ASTM C204
Initial setting time (Hours)	2.30	ASTM C191
Final setting time (hours)	4.15	
Soundness	0.19	ASTM C151
Compressive strength (3-days), MPa	14.96	ASTM C109
Compressive strength (7-days), MPa	20.80	

3.1.2. Coarse and Fine aggregates

Coarse and fine aggregates were collected from Leghar Coarse and fine aggregates supplier, which is local resource and are a good quality crushed stone and river sand, respectively. The size of coarse aggregates were 19 mm, 9.5 mm and 4.75 mm and fine aggregates were 4.75 mm, 2.36 mm, 1.18 mm, 600 µm, 300 µm and 150 µm.

Before, incorporating into concrete mix, these ingredients were washed with pure water to make free from adherent coating, injurious amount of disintegrated pieces, alkali, organic matter and other deleterious substances and then, dried by air.

3.1.2.1. Water absorption of coarse aggregate

The durability and mechanical strength of concrete materials highly depends on the water to cement ratios. The increased water to cement ratio, results in a decreased concrete strength. Most of the time, aggregates have limitation to meet the standards of expected quality due to either absorbing water or by releasing it to the mix.

Therefore, it is imperative to determine absorption capacity of the aggregate. In this thesis, the water absorption of aggregate was determined, by weighing 5000 g of coarse aggregates and submerging in water for 24 hrs. And then, dried the surface with cloth and, then weighted the weight of the CA i.e. Saturate Surface Dry, SSD. After that, oven dried for 24hrs and, the oven dried (OD) weight at a temperature of 110 ^{o}C has been measured and then, the weight difference divided by the oven dried weight and then, multiplied by 100.

3.1.3.2. Unit weight of bulk coarse aggregate

In order to determine the unit weight of bulk coarse aggregate, 26,835 g of coarse aggregate has been measured by cylindrically shaped container. The height of sample container was 28cm and the radius was 26 cm. Therefore, using these numerical values, volume of cylinder will be determined.

3.1.3. 3. Moisture content of Coarse Aggregate

In order to determine the moisture content of the coarse aggregate, 1000gm of CA has been measured and then, oven dried for 24 hrs and, weighted. The results will be obtained through applying mathematical calculations that found in results and discussion part of the study.

3.1.3.4. Specific gravity and absorption capacity of Fine Aggregates

Specific gravity is an expression of the density of an aggregate. Aggregates contain pores in their structure, therefore the specific gravity depends on whether the pores are included in the measurement or not.

In order to determine the specific gravity and absorption capacity of fine aggregates manual exist in Material Testing has been applied. The apparent specific gravity of an aggregate denotes to the solid materials without the pores and bulk specific gravity refers to total volume i.e. including pores of the aggregate.

3.1.3.5. Silt test of fine aggregate, FA

In order to determine the silt content of FA, measuring cylinder filled with water up to 300 ml, has been used. Then, 500 g of FA has been added to it and the volume reached to 800 ml and then, shaked well and, finally salt added over it to make the boundary separation very well.

After 5hrs, the boundary between sand and silt has been well identified. To determine the silt content, the amount of silt over sand has been identified and to be represented by V_1, and the sand volume has identified and to be represented by, V_2.

3.1.4. TiO_2 Nano-Particle (TNP)

In order to solve cracking problems of concrete structure, the Anatase form of TNP with 99.9% purity and 5 nm scale was obtained from Sky-Spring Nano-materials, Inc.

The wt. % of TNP substitution was (0%, 0.5%, 1%, and 1.5%). The concrete produced with very small dosage of TNP has improved strength and durability properties (Xu, Xie et al. 2018). According to the study of (Xu, Xie et al. 2018), small amount of nanoparticles was used to prevent the agglomeration of nanoparticles, and hence, to improve the mechanical strength and durability properties.

As the investigation made by (Zhang and Zong 2014) showed that, the TNP incorporated into concrete to improve the brittle nature of CCMs, mechanical strength, integrity, bond strength, toughness, fatigue resistance and fluid permeability.

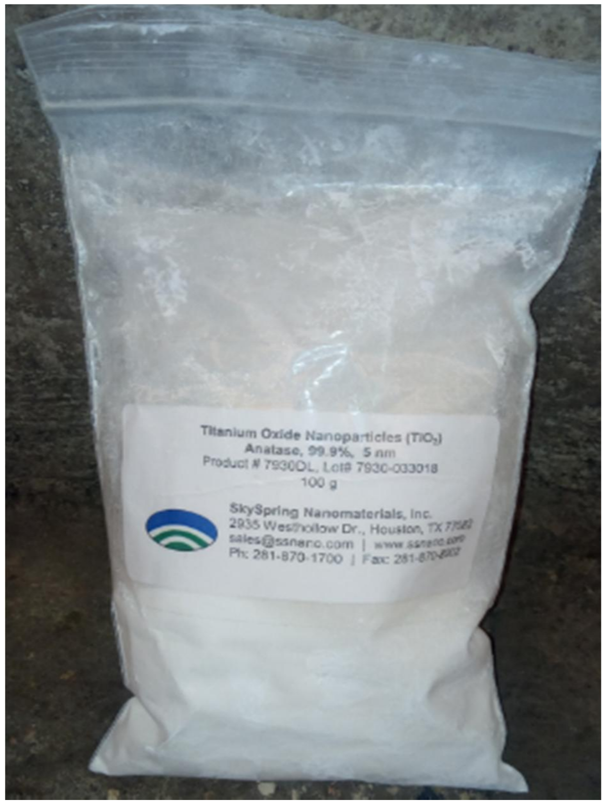


Figure 3.1: Packed Anatase form of TiO_2 nanoparticles

3.1.5. Waste Plastic Fiber (WPF)

The incorporation of WPF is envisioned to improve the genetic defects of cement based materials including high brittleness, and internal cracks, which lead to a decline in performance and service life of building materials and road infrastructures. The substitution of fibers mostly suggested arresting the cracks by forming bridges across micro and macro cracking in concrete structures.

The choice of waste PET bottles was due to its promising properties, and high consumption of beverage and packaged drinking and highly disposed in everywhere and has huge impacts in environmental pollution (Pereira, de Oliveira Junior et al. 2017). The sand material partial replacement was to save depletion of virgin material without compromising the quality of concrete and to keep away the shortage of river sand in the near future (Vishwakarma and Ramachandran 2018).

The replacement of waste PET bottle with sand was by wt. % of (0%, 0.2% and 0.4%), which was collected from Addis Ababa Institute of Technology compound, and grinding process was accompanied by Ethio-plastic manufacturing industry by using TRIA, ANCESCHI & FIGLI S.R.L, grinding machine, new version. The size reduction of PET material is not as such much simple. However, using new version grinding machine, the size reduced to the range of 3 mm to 5 mm, which is appropriate size to substitute FA. The grinding process of PET bottles was schematically represented by fig 3.2.

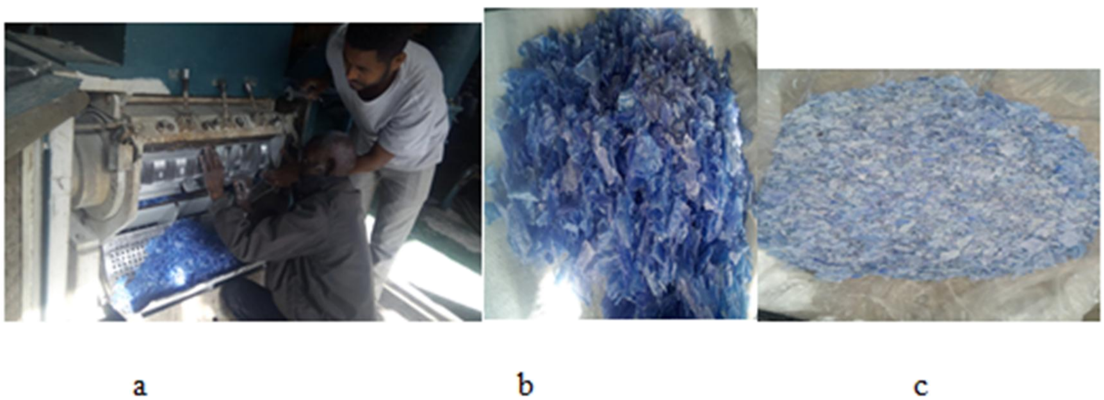


Figure 3.2: Grinding waste PET bottles (a), un-preferential size of PET bottles (b) and PET bottles grinded with preferential size to substitute sand (c)

3.1.6. Admixtures

For the sake of workability and well dispersion of TNP, 505 Ethio-plast super plasticizer admixtures have been incorporated in concrete mix with the same proportions. The physical properties of the Super Plasticizer (SP) – high range water reducer and set accelerator have liquid nature, dark brown color, density of 1.220 ± 0.020, PH value of 7± 2 added in all mixtures.

The standard specifications of admixtures conforms ASTM C-494 Type A and F and it is a polynapthalene based synthetic polymer. In each concrete mix, 10ml super plasticizer has been added.

3.1.7. Water

The quality of water is very important, because contaminants can adversely affect the strength of concrete and cause corrosion of the steel reinforcement. Water used for producing and curing concrete has been reasonably clean and was free from any deleterious substances such as oil, acid, alkali, salt, sugar, silt, organic matter. Therefore, portable tap water that is safe for drinking is used.

3.2. Methods

3.2.1. TNP and WPF Modified Concrete

To prepare concrete materials, that contains TNP, 505 Super Plasticizer has been firstly mixed with water in a mixing bath, and then, TNP has been added and stirred at a high speed for 5minutes. The other raw ingredients, such as coarse aggregate, fine aggregate and grinded waste PET bottles and cement were mixed separately, at a low speed in a concrete blender, and then, the mixture of water, super plasticizer and TNP have been slowly poured into concrete blender, and automatically stirred at for about 7 minutes to achieve proper workability (N. Salemi et al, 2014).

Finally, the fresh concrete has been poured into oiled molds to form concrete samples. Then, an external vibrator is used to enable compaction and lessening the amount of air bubbles. The specimens was demolded after 24 hrs and then, cured in a water bath in material test lab and dried at a room temperature.

3.2.2. Unmodified/Conventional Concrete

To prepare CCMs, 505 super plasticizer has been firstly dissolved in water and then, the separately prepared coarse and fine aggregates, and cement were mixed uniformly in a concrete blender, and then, the mixture of water and super plasticizer have been poured into concrete blender and stirred for 5minutes (N. Salemi et al, 2014).

Finally, the fresh concrete has been poured into oiled molds to form concrete samples. Then, an external vibrator was used to enable compaction and lessening the amount of air bubbles. The specimens was demolded after 24h and then, cured in a water bath in material test lab and dried at a room temperature.

Chapter Four: Experimental Part

4.1. Experimental Mix Design

Mix design of concrete samples has prepared to evaluate the mechanical strength, durability properties like, water impermeability properties with partial replacement of cement and sand with TNP and WPF, respectively. In the process of preparing mix design of concrete samples, water to cement ratio (W/C), is critical to achieve desired strength and durability properties. As indicated in table 4.1, the W/C of mix design used is 0.54. Lower W/C ratio was used to increased strength and durability properties.

The concrete samples of modified and unmodified are given in table 4.1. The samples has prepared using mold of 150 mm X 150 mm for cubic concrete and 150 mm X 300 mm used for cylindrical concrete samples.

Table 4.1: Mix Design of concrete samples

Sample name	OPC (kg/m^3)	TNP(kg/m^3)	Water (kg/m^3)	FA(kg/m^3)	CA (kg/m^3)	WPF (kg/m^3)	505 SP (ml)
CCM	364.62	0.00	196.9	948.56	1097.3	0.00	10.00
TNP0.5+WPF0.2	362.79	1.84	196.9	946.67	1097.3	1.896	10.00
TNP0.5+WPF0.4	362.79	1.84	196.9	944.77	1097.3	3.79	10.00
TNP0.5	362.79	1.84	196.9	948.56	1097.3	0.00	10.00
TNP1	360.98	3.64	196.9	948.56	1097.3	0.00	10.00
TNP1.5	359.14	5.48	196.9	948.56	1097.3	0.00	10.00

There are totally 6 concrete mix types with a constant water/cement (w/c) ratio of 0.54 and, the OPC used in each of mix types are 364.62 kg/m^3, 362.79 kg/m^3 (3), 360.98 kg/m^3 and 359.14 kg/m^3. Concrete samples have been prepared without and with partial replacement of OPC with wt. % of (0, 0.5, 1 and 1.5) of TNP & sand with wt. % of (0, 0.2 and 0.4) of WPF. The concrete materials preparation, mixing of ingredients, and samples prepared are schematically represented in fig 4.1 below.

a b

c

Fig 4.1: a) Different raw material mix together in mixer b) Materials well mixed in mixer c) Different concrete specimens prepared

4.2. Experimental Procedures of concrete preparation

According to the ASTM C-192, concrete samples were prepared by applying the following procedures and activities.

i. Collecting each ingredient required for concrete preparation.
ii. Adjusting place that suit to the ingredients behavior.
iii. Testing the properties of ingredients to fit the desired properties of concrete.
iv. Arranging all the ingredients separately with respect to required amounts.
v. Designing mix ratio of each ingredient for concrete samples preparation.
vi. Mixing all raw ingredients together in a mixer and
vii. Prepare all molds of 150 mm X 150 mm and 150 mm X 300 mm cubes and cylindrical shape concrete, respectively.
viii. Oiling all the molds to easily remove the samples after 24 hrs.
ix. Testing the consistency of fresh concrete samples, slump test.
x. Filling the concrete molds with freshly prepared concrete samples.

The concrete specimens was kept in molds for 24 hrs to gain shape of the mold and then, removed and immersed in water bath for curing.

Total of 114 concrete specimens were produced. Among which, 54 concrete cubes were for compressive strength test and 6 samples were to test water permeability whereas, 54 concrete cylinders were assigned for splitting tensile strength test after curing for 3, 7 and 28 days.

4.3. Curing and Testing

According to the ASTM C-39, the concrete samples were dried in moist room before test and then, the weight of concrete specimens were measured. The compressive strength, splitting tensile strength and water permeability tests have been conducted and, then the average of each concrete mix at the same age has been determined.

4.4. Concrete Specimens

4.4.1. Concrete Specimens for Compressive Strength Test

The total numbers of concrete specimen for compressive strength test were reported in table 4.2. The compressive strength of concrete is used to determine the compression resistance of concrete materials during service provision.

Table 4.2: Concrete samples for compressive strength test

S.no	Cubes specimen (150mmX150mm)	Total No of specimens	Days of testing			Composition of TNP and WPF %
			3	7	28	
1	Only TNP modified	27	9	9	9	(0.5, 1 & 1.5)
2	Both TNP & WPF modified	18	6	6	6	(0.5 & 0.2, 0.5 & 0.4
3	Unmodified	9	3	3	3	(0 & 0)
Total		54	18	18	18	

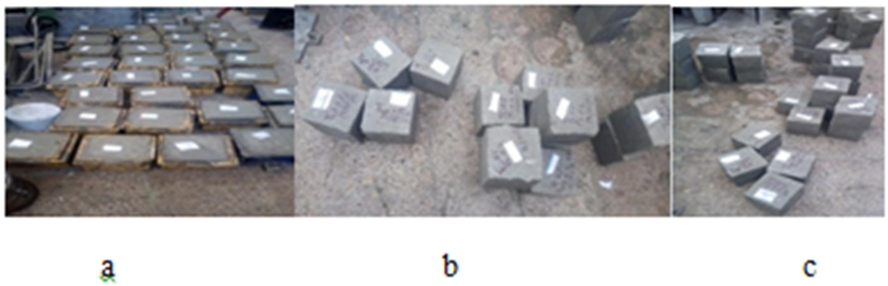


Figure 4.3: concrete specimen in the mold (a), cured for 3 days test (b) and cured for 7 days test (c) and cured for 28 days test (d)

4.4.2. Concrete specimens for splitting Tensile Strength Test

To investigate the splitting tensile strength of concrete specimens after 3, 7 and 28 days of curing, totally 54 concrete samples have been prepared. The 3, 7 & 28 days testing concrete has been found in table 4.3.

Table 4.3: Cylindrical Concrete samples for splitting tensile test

S.no	Cylindrical specimen (150 X 300) mm	No of specimen	Days of testing			Composition of TNP and WPF%
			3	7	28	
1	Only TNP modified	27	9	9	9	(0.5, 1 & 1.5)
2	Both TNP & WPF modified	18	6	6	6	(0.5 & 0.2, 0.5 & 0.4
3	Unmodified	9	3	3	3	(0 & 0)
Total		54	18	18	18	

Figure 4.4: Concrete samples for splitting tensile test

4.4.3. Water Permeability (Durability Test)

The water absorption of concrete samples will be assessed, after 28 days of curing. The concrete cubes were dried at 25 ^{o}C for 7 days in air. Then, each concrete cubes were submerged into a water-absorption apparatus. At the beginning of the experiments, the initial masses of concrete cubes were measured and, represented by (M_i).

The concrete cubes were submerged in water absorption apparatus for 72 hrs(3 days). After 72 hrs, the concrete cubes were removed from the water-absorption apparatus and then, the surface of concrete was dried in air for 20 minutes. Afterwards, the mass of the concrete cube has been weighed, and represented by (M_f).The weight loss of each concrete cubes will be determined by using the following equation,

Weight loss of concrete samples in (%) = $(M_f - M_{i.})/M_{i.}$ *100. The concrete samples prepared for water absorption test found in table 4.4.

Table 4.4: Concrete cubes prepared for water permeability test

S.no	Cubes specimen (150 X 150) mm	No of specimen for water permeability	Composition of TNP and WPF%
1	Only TNP modified	3	(0.5, 1 &1.5)
2	Both TNP & WPF modified	2	(0.5 & 0.2, 0.5 & 0.4
3	CCM	1	(0 & 0)
	Total	6	

4.5. Scanning Electron Microscope (SEM) Technique

The SEM analysis is conducted to observe the microstructure (morphology) of unmodified and modified concrete. Modifications in the morphology of modified concrete with both TNP and WPFs, and only modified with TNP have been investigated and then, the results have been compared with the unmodified concrete, CCMs.

Several investigations regarding the incorporation of Nanoparticles indicate that the nanoparticles are uniformly dispersed can act as a filler to improve the density of concrete. Due to this fact, the porosity of concrete significantly reduced (Jalal, Mansouri et al. 2012).

To observe the modification in the morphology of concrete; the samples cured for 28 days have been analyzed. Previously conducted research works indicated that 28 days cured concrete properties have assured the whole concrete properties modification. To investigate the concrete properties with SEM technique, samples have been selected from all types of concrete mix of 28 days cured, i.e., from both (0.5 % TNP + 0.4 % WPF) modified concrete, only 1.0 % TNP modified concrete and unmodified concrete samples. For the analysis, concrete cubes have been dried for three days in the air and then crashed with steel. After that,15 g has been taken from the core parts of each sample prior to milling and then automatically sieved with a 32 µm scale sieve.

4.6. X-Ray Diffraction (XRD) Technique

The XRD technique is used to investigate the crystal structure, and phases that exist in concrete samples. Samples have been selected from concrete materials modified with both TiO_2 nanoparticles and waste plastic fibers, only with TiO_2 nanoparticles modified and unmodified concrete. To proceed the experimental activities, the cubes have been dried and crashed. A small piece of concrete has been taken from the center and then finely ground. The sample has dried and, finally, sieved with 32 µm scale mesh.

XRD test has been conducted at Adama Science and Technology University (ASTU, Ethiopia). The XRD experiment was conducted with 15 g of a sample using X-ray diffractometer with an X - Ray source of Cu (K-alpha), over a 2Θ range of $10 – 80^o$ at continuous scan mode with a scan speed of 4.00 deg/min. The X-Ray tube voltage and current fixed at 40 kV and 30 mA, respectively. The presence of various types of crystalline phases in the specimens has been identified through the standard database for X – Ray Powder diffraction pattern.

4.7. Differential Scanning Calorimetry - Thermo-Gravimetric Analysis (DSC-TGA)

DSC-TGA tests were carried out to identify the maximum weight loss in samples at a given temperature range. The weight loss difference in both unmodified CCMs) and modified concrete with TNP and WPF was compared.

The test samples were prepared from both unmodified and modified concrete, which were taken from 28 days of curing. The concrete cubes have been dried, crashed, powdered and small pieces of concrete has been taken from the core part of concrete to carry out the test. Then, the finely ground powder has been dried and sieved with a 32 µm scale siever.

Hence, the concrete samples have been taken to Leather Industry Development Institute (LIDI, Addis Ababa, Ethiopia) and the The samples were heated from ambient temperature to 800 °C under nitrogen environment, at a heating rate of 10 °C/min.

Chapter Five: Results and Discussion

In this chapter, results obtained from the experimental activities have been presented, analyzed, and interpreted with details. The analysis of the test results was intended to indicate, the differences found in modified and unmodified concrete samples. The differences between modified and unmodified concrete with respect to mechanical strength and durability properties were evaluated. Furthermore, it is very important to remain mindful to the facts of the experimental sections results related to the facts reviewed in the literature.

5.1. Sieve Analysis of Fine and Coarse Aggregates (sand)

In order to determine the size of fine aggregate, 500 g of fine aggregate was measured, washed and then, kept in oven drier for 24 hrs. After 24 hrs, it was removed from the oven and then, cooled by keeping in fresh air before sieving analysis takes place. Figure 5.1 shows, the process performed; oven drying, cooling and finally, analyzing. As reported in table 5.1, it was possible to observe various sieve size, weight of fine aggregate retained, and their cumulative % weight determined.

a b c

Figure 5.1: Preparation of FA sieve analysis

Oven drying for 5hrs (a) Cooling FA (b) Sieving of FA with different sieve size (c)

The Fineness Modulus of fine aggregate was determined by summing up all the cumulative percentage retained and divided it to 100. Therefore, the fineness modulus of the aggregate used is 2.65. The Fineness Modulus figure is found in acceptable range.

Table 5.1: Sieve analysis of FA

Weight of fine aggregate = 500				
Sieve size	Weight retained(g)	% Retained	Cumulative %Retained	Cumulative % passing
9.5mm	0.00	0.00	0.00	100.00
4.75mm	1.50	0.30	0.30	99.70
2.36mm	38.00	7.60	7.90	92.10
1.18mm	75.90	15.18	23.08	76.92
600µm	140.90	28.18	51.26	48.74
300µm	167.60	33.52	84.78	15.22
150µm	66.80	13.36	98.14	1.86
pan	9.30	1.86	100.00	0.00
Total	500.00	100.00	265.46	
✓ The fineness modules of FA is 2.65				

The weight of fine aggregates, and their cumulative percentage retained have been represented graphically in figure 5.2.

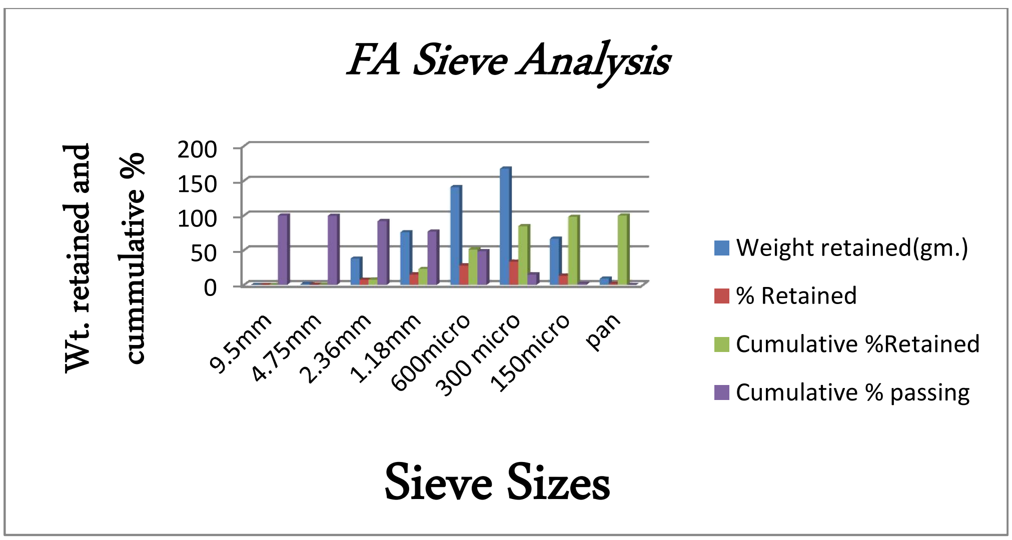


Figure 5.2: Graphical representation of sieve analysis of FA

In order to determine the size of coarse aggregate, 5000gm of sample has been weighed, and then washed with water, and put in oven drier for 24 hrs. After 24 hrs, it has been removed and then cooled before sieving process take place with sieve sizes from 75 mm to 4.75 mm.

The retained weight and their cumulative percentage of coarse aggregates in each sieve size found in table 5.2. The Fineness Modulus of coarse aggregates determined was 2.57.

Table 5.2: Sieve analysis of CA

Weight of Coarse aggregate = 5000g				
Sieve size	Weight retained(gm.)	% Retained	Cumulative %Retained	Cumulative % passing
75mm	0.00	0.00	0.00	100.00
37.5mm	0.00	0.00	0.00	100.00
19mm	2875.00	57.50	57.50	42.50
9.5mm	2086.00	41.72	99.22	0.78
4.75mm	39.00	0.78	100.00	0.00
Pan	0.00	0.00	100.00	0.00
Total	5000.00	100.00	256.72	
✓ Fineness modulus of CA is 2.57				

The wt. retained and their cumulative percentage in each sieve size was showed in figure 4.3.

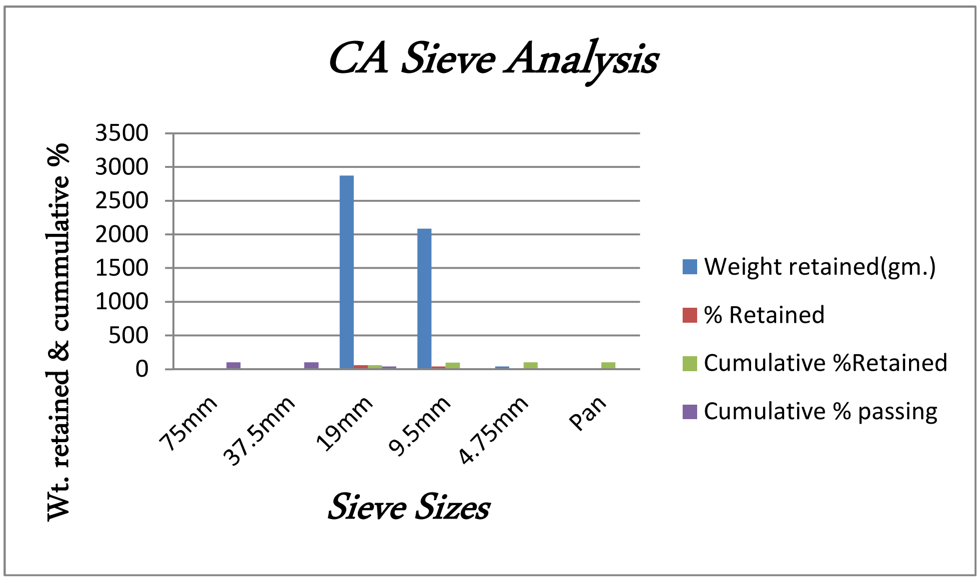


Figure 5.3: Sieve analysis of CA

5.1.2. Water absorption of coarse aggregate

To determine the water absorption capacity of coarse aggregates, the experimental activities has been performed and the following results was obtained.

Weight of Surface Saturated Dry Test Sample (SSD) = 4987.3gm

Weight of oven dried test sample (OD) = 4938.3gm

Water absorption % = ((SSD-OD)/OD)*100= ([4987.3-4938.3]/4938.3*100= 0.99%.

5.1.3. Moisture Content of Coarse aggregate

Moisture content (%) = (Original CA - OD/OD) *100,

= (1000 – 994.3)/994.3 = 0.57 %

5.1.4. Specific gravity and absorption capacity of Fine Aggregates

Weight of original sand Sample = 300gm

Wt. of pycnometer =W= 212.1gm

Weight of pycnometer + weight of sand sample = 512.1gm

Weight of pycnometer + sand + water = C = 905.6gm

Weight of oven dried sand sample = A = 284.7gm

Wt. of pycnometer filled with water =B =0.9976V + W=0.9976 gm/ml*500 ml + 212.1gm=710.9

V = volume of pycnometer = 500ml

W = wt. of pycnometer empty = 212.1gm

Bulk specific gravity = A/B+300-C = 284.7/710.9+905.6 = 1,206 g/m^3

A = Oven dried sand sample

B = Wt. of pycnometer filled with water

C= Weight of pycnometer + sand + water

Bulk spec gravity (Saturated surface dry base) = 300/B+300-C = 300/710.9+300-905.6= 2.85

Apparent specific gravity = A/B+A-C= 284.7/710.9+284.7-905.6 = 3.16

5.1.5. Moisture Content of fine aggregate

Weight of test sample before Oven Dry (gm.) (OD_1) =500 gm

Weight of test sample After Oven Dry (gm.) (OD_2) = 481.5gm.

Moisture Content = (OD_1-OD_2)/OD_2 = (500 – 481.5)/ 481.5 = 3.8%

5.1.6. Silt Content

Silt content % = [silt content, V_1/ sand content, V_2]*100

Silt content (%) determination, before washing the fine aggregate

Total volume occupied by fine aggregate and silt in measuring cylinder= 310ml

Content of silt over sand in measuring cylinder= 18ml

Content of fine aggregate in measuring cylinder = 292ml

Silt content % = [310ml – 292ml]/292ml *100 = 6.8%

The silt content % in fine aggregate is greater than the permissible percentage, since it is greater than 6%.

Therefore, washing of fine aggregate is mandatory and after washed, the silt content % is determined and it becomes 4.5%, which is in range of permissible. Silt content % determination, after washing the fine aggregates.

Total volume occupied by sand and silt = 230ml

Content of silt over sand = 10ml

Content of sand = 220ml

Silt content % = [230ml – 220ml]/220ml *100 = 4.5 %

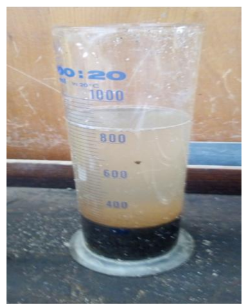


Figure 5.4: Silt content determination

5.1.7. Unit weight of Coarse Aggregate

V = $\pi.r^2.h$ = 3.14*13cm*13cm*28cm = 14,858.48cm^3

Unit wt. of bulk coarse aggregate = 26,835g

Density of coarse aggregate = 26,835g/14,835cm^3 = 1,808kg/cm^3

Table 5.3: Summary of test results of aggregates

S.no	Test Description		Test Result
1	Silt Content		4.5 %
2	Moisture Content of fine aggregate		3.8 %
3	Moisture content of coarse aggregate		0.57 %
4	Unit wt. of Coarse aggregate		1,808 kg/cm^3
5	Water absorption Cap.		0.99 %
6	Specific gravity of FA	Bulk, Kg/cm^3	1.2 kg/m^3
		Bulk (SSD)	2.85
		Apparent	3.16
7	Fineness Modulus	CA	2.57
		FA	2.65

5.1.8 Particles Size Distribution of OPC & TNP

As the table 4.4 shows, sieving of OPC and TNP were conducted through different seiver scales. Hence, in 300 µm scale siever 98.5% OPC passed, whereas 100 % TNP passed. Similarily, in 150 µm siever 79.7 % OPC were passed, whereas 100 % TNP passed. In 75 µm siever, 76.4 % OPC and 100 % TNP has passed, but in 32 µm seiver scale 49.1% OPC and 100 % TNP has passed.

Therefore, the particle size distribution of OPC and TiO_2 nanoparticles were sieved with seiver scale range from 300 µm to 32 µm. But, important thing to remember here is TiO_2 material is in nano-scale and 100 % of it has passed with the micro-scale measurements.

Table 5.4: Particles size distribution of OPC and TNP

Sieve size	Retained gram (OPC)	Cumulative % passing	Retained g (TNP)	Cumulative % passing
600 µm	0	100	0	100
300 µm	1.5	98.5	0	100
150 µm	20.3	79.7	0	100
75 µm	23.6	76.4	0	100
32 µm	50.9	49.1	0	100

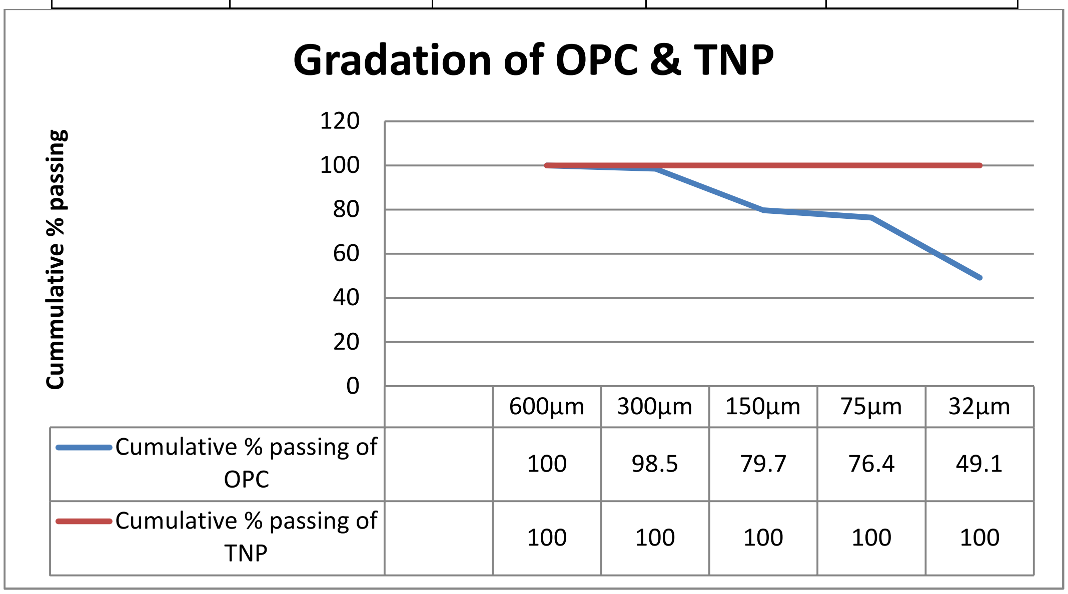


Figure 5.5: Gradation of OPC & TNP

5.2. Workability of Concrete

The workability test was performed mainly to observe the consistency of concrete mix in each concrete batch. Therefore, the slump test has been applied to observe the consistency in each concrete batch. The slum test measured the consistency of freshly made concrete before it sets. It helps to check the workability of freshly made concrete.

The property of concrete is affected by a number of factors such as water content of the mix, mix proportions, aggregate properties, time, characteristics of the cement and admixtures. Increasing the amount of water will increase the workability of the concrete; however, the increase in water content will decrease the strength and, also result in segregation.

The slum test is carried out using a metal mold in the shape of a conical frustum known as a slump cone, which is open at both ends and has attached handles. The cone is put on a hard non-absorbent surface. This cone is occupied with fresh concrete in four stages. The slump of the concrete is measured by computing the distance from the top of the slumped concrete to the level of the top of the slump cone. The slump test is carried out as per procedures stated in ASTM C-143. All the batches of freshly made concrete has the slump test in range of 45 – 60 mm and which, shows a good workability of concrete mix.

Figure 5.6: Slump test

5.3. Mechanical Tests

5.3.1. Compressive Strength Test

The compressive strength test has been conducted, according to the ASTM C-109 after curing for 3, 7 and 28 days. The compressive strength of all concrete samples unmodified, modified with TNP and WPF has been tested. All of modified concrete samples compared with unmodified showed an advanced strength modifications. But, maximum compressive strength improvement was achieved through the incorporation of both TNPs & WPFs in compositions of (0.5 % TNP + 0.2 % WPF) and (0.5 % TNP + 0.4 % WPF). However, extremely large compressive strength improvement was attained through the compositions of (0.5 % TNP + 0.4 % WPF) modified concrete. The partial substitution of cement with TNPs accelerated the hydration reactions mainly of the reaction between C_3S & C_2S with water, since they are the major components and their reaction generated additional C-S-H gels, strength improving components in concrete. Well dispersed TNPs incorporated in concrete properties were improved through providing a dense and compacted microstructure through filling effects.

The incorporation of WPF has improved the toughness, ductility, and fracture resistance of concrete materials. To build durable and resisting fracturing of structure due to various external conditions and enhancing performance before designing high rise and large span structure were critical issue. For that matter, promising materials that could improve compressive strength were in need.

In addition, the filling effects of TiO_2 nanoparticles and WPFs, has improved the bond strength and integrity between cement paste and aggregates in concrete structure. Therefore, these filling effects made the microstructure to be denser, compacted, and made to obtain improved compressive strength than unmodified concrete. This densified microstructure has reduced growth space of CH crystals, and thus the size of CH crystals within concrete structure becomes reduced.

The average compressive strength of 3, 7 and 28 days results has been reported and discussed in details. The compressive strengths of 3 days cured for unmodified concrete was 17.3 MPa as reported in table 4.5. This compressive strength result was very low compared with modified concrete. The partial replacement of concrete modifiers, like TiO_2 nanoparticle has facilitated the hydration reaction kinetics uniformly, created nucleation sites and generated additional hydration products like C-S-H gel, which improved the concrete properties. The average compressive strength of modified and unmodified concrete samples of 3, 7 and 28 days of curing and their corresponding percentage improved have been found in table 5.5.

Table 5.5: Compressive strength & their corresponding % enhanced

Mix code	Compressive strength of concrete, MPa					
	3 Days	%, Enhanced	7 Days	%, Enhanced	28 Days	%, Enhanced
CCM	17.3	0.00	22.06	0.00	29.01	0.00
TNP0.5+WPF0.2	23.59	36.40	29.60	34.18	37.50	29.27
TNP0.5+WPF0.4	31.57	82.48	34.28	55.39	39.05	34.61
TNP 0.5	27.95	61.56	29.79	35.04	34.29	18.2
TNP 1	29.53	70.69	30.76	39.44	36.86	27.06
TNP 1.5	28.96	67.39	28.32	28.37	30.66	5.69

The compressive strength of 3 days modified with (0.5% TNP + 0.2% WPF) showed 23.59 MPa, which was 36.42 % modified than unmodified concrete. The concrete modified with (0.5 % TNP + 0.4 % WPF) showed 31.57 MPa, which was 82.48 % modified than CCMs, this indicated almost doubled the CCM strength. The Concrete modified with only TNP with (0.5% TNP) showed 27.95MPa,which was 61.56 % modified than unmodified concrete. But, the concrete modified with (1 % TNP) showed 29.53MPa which was 70.69 % modified than unmodified concrete. The concrete modified with (1.5% TNP) showed 28.96MPa, which was 67.39% modified compared to unmodified concrete.

The strength modification from 1 % TNP to 1.5 % TNP is 3.3 % reduced, this was due to agglomeration problem. Above a certain proportions nanoparticles incorporation has negative impacts i.e. the nanoparticles became agglomerate, and forms a more porous structure, and thus losses the positive effect on improving the concrete materials.

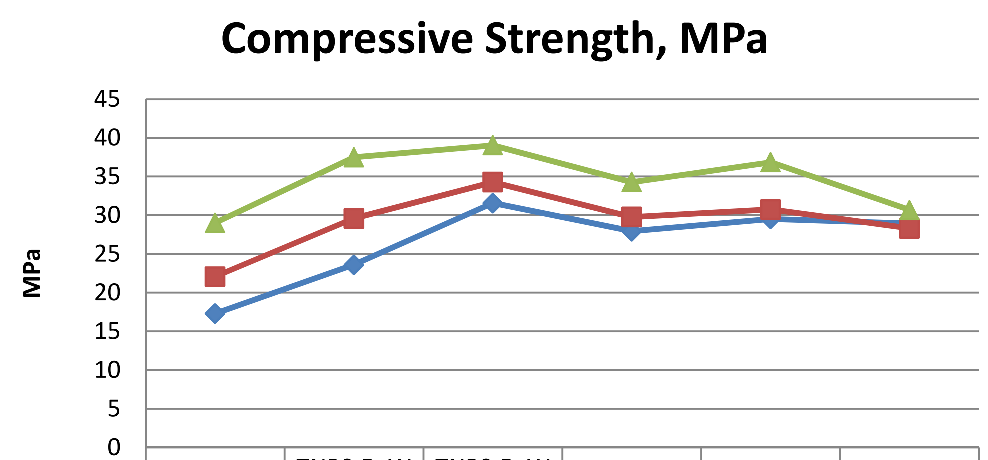
The compressive strength of 7 days cured unmodified concrete, the test result indicated 22.06 MPa. But, the concrete modified with (0.5 % TNP + 0.2 % WPF) showed 29.6 MPa, which was 34.18% modified than CCMs, and the concrete modified with (0.5 % TNP + 0.4 % WPF) showed 34.28 MPa,which was 55.39 % modified. The concrete modified with (0.5 % TNP) showed 29.79 MPa, which was 35.04% modified, and the concrete material modified with (1 % TNP) showed 30.76 MPa,which was 39.44 % modified than unmodified concrete. The concrete modified with (1.5 % TNP) showed 28.32MPa,which was 38.38 % modified than unmodified concrete. Therefore, the concrete modified with 1.5 % TNP was reduced by 1.06 % compared with unmodified concrete.

When the compressive strength of 7 days cured concrete compared with the 3 days cured, there was better strength increment in all concrete types. The reasons behind the improvement were due to the cement hydration process led to extra generation of C-S-H gels than the 3 days. Since, some additional C-H converted into C-S-H gels and also, C_3S & C_2S reaction facilitated to form extra hydration product C-S-H gel & CH, due to the presence of TNP and increased integrity between cement paste and the aggregates. In addition to TNP, the incorporation of WPFs increased the aggregation between the components.

The compressive strength of 28 days cured unmodified concrete test results indicated 29.01 MPa. However, the concrete material modified with (0.5 % TNP + 0.2 % WPF) showed 37.50 MPa,which was 29.27 % modified than unmodified concrete, and when compared with the 7 days result, it is 7.90MPa increased. The compressive strength of (0.5 % TNP + 0.4 % WPF) modified concrete showed 39.05 MPa,which was 34.61 % modified than unmodified concrete and when compared with7 days, it is 4.77 MPa increased. The concrete modified with (0.5 % TNP) showed 34.29 MPa , which was 18.20 % modified than unmodified concrete, and when compared with the 7 days, it is 4.5 MPa increased, the concrete modified with (1 % TNP) showed 36.86 MPa,which was 27.06 % modified than unmodified concrete and when compared with 7 days result, 6.1 MPa increased. The , concrete modified with (1.5 % TNP) showed 30.66 MPa,which was 5.69 % modified than unmodified and, when compared with the 7 days, it is 2.34MPa increased.

However, when compared the 1%TNP & 1.5%TNP modified concrete of 28 days cured, 1.5 %TNP modified reduced by 6.2 MPa, which was 21.37 % reduced). This was due to the agglomeration of nanoparticles, and forming a more porous structure, and thus losses the positive effect on improving the concrete materials.

The compressive strengths of modified and unmodified concrete samples of 3, 7 and 28 days cured has been found in figure 5.7.



	CCM	TNP0.5+WPF0.2	TNP0.5+WPF0.4	TNP 0.5	TNP 1	TNP 1.5
3d	17.3	23.59	31.57	27.95	29.53	28.96
7d	22.06	29.6	34.28	29.79	30.76	28.32
28 d	29.01	37.5	39.05	34.29	36.86	30.66

Figure 5.7: Compressive strengths of 3, 7 & 28 days of curing

The partial replacement of cement with TiO_2 nanoparticles and sand with waste plastics fiber has improved the compressive strength indeed. As the authors (Mustafa, Hanafi et al. 2019) investigation assured that, the incorporation of waste plastic fiber have significant effects on development of compressive strength and stress resisting behavior of concrete materials. As the experimental results of (Ceran, Şimşek et al. 2019) affirmed that, the incorporation of smaller particles form a more compacted structure and can improve the compressive strength of concrete.

As the investigation made by (Diab, Elyamany et al. 2019) revealed that, the modifications of compressive strength with nanoparticles is mostly due to the filling effects of nanoparticles. Although there are various research works, which assured the advantages of nanomaterials in improving concrete properties like compressive strength and tensile strengths and water, chloride and other chemicals through the filling effects.

The results obtained in experimental works of this thesis was agreed with the investigation made by (S. XU et al. 2018), i.e. the average compressive strengths of the control sample was about 32.5 MPa, while modified with TiO_2 nanoparticles increased to 36.8 MPa, with incorporation of 1 wt. % TiO_2 nanoparticles. The results obtained through the incorporation of (0.5%TNP and 0.4 % WPF) have 39.05 MPa. This experimental result indicated that; the incorporation of both TNP & WPF has greater strength modification than only nanoparticles.

a b c

Figure 5.8: Testing of compressive strength of modified (a), modified with both TNP & WPF (b), & only TNP modified concrete (c)

The standard deviations of the 3, 7 and 28 days of curing time for average compressive strength of concrete material has been determined. The mix number, average compressive strength (MPa), and standard deviations for all 54 concrete material found in table 5.6 below.

Table 5.6. Compressive strength test results and their standard deviations.

Mix Number	3-day average compressive strength, (MPa)	Standard deviation of 3 replicates of each mix (MPa)
1	17.3	0.286
2	23.59	2.32
3	31.57	0.036
4	27.95	0.35
5	29.53	0.035
6	28.96	0.06
	7 days average compressive strength, (MPa)	
1	22.06	1.483
2	29.60	0.1
3	34.28	1
4	29.79	1
5	30.76	1.02
6	28.32	1.07
	28-day average compressive strength, (MPa)	
1	29.01	1.33
2	37.50	3.05
3	39.05	2.03
4	34.29	1.33
5	36.86	2.13
6	30.66	2.31

5.3. 2. Splitting tensile strength test

The partial replacements of TNP and WPF with cement and sand respectively, have increased their splitting tensile strength for all the test days (see figure 4.9). Due to these modifiers concrete properties like splitting tensile strength, ductility, toughness, and fracture resistance has improved. Improving the ductile behavior of concrete could be very beneficial in minimizing crack formation capability in concrete structures.

Improving of splitting tensile strength was due to the accelerations of early cement hydration process and dissolution of CH and hence, generation of additional C-S-H gels. The WPF incorporation has improved the prevention of crack initiation and propagation, bridging effects in macro and micro cracking, redirects the crack path, restrain and delay crack growth rate within concrete structure. Therefore, the concrete split tensile strength has increased.

The splitting tensile strength of 3 days cured unmodified concrete; showed 3.98 MPa. But, the concrete modified with (0.5 % TNP + 0.2 % WPF) showed 4.76 MPa, which was 19.59% modified than unmodified concrete. The concrete modified with (0.5%TNP + 0.4%WPF) showed 5.74MPa,which was 44.22% modification than unmodified concrete. And, concrete modified with (0.5%TNP) showed 4.58MPa,which was 15.07% modified than unmodified concrete. Concrete modified with (1%TNP) showed 5.06MPa,which was 27.14% modified and concrete modified with (1.5%TNP) showed 4.97MPa,which was 24.87% modified than unmodified concrete. However, the splitting tensile strength slightly reduced from 1%TNP to 1.5%TNP due to agglomeration effects.

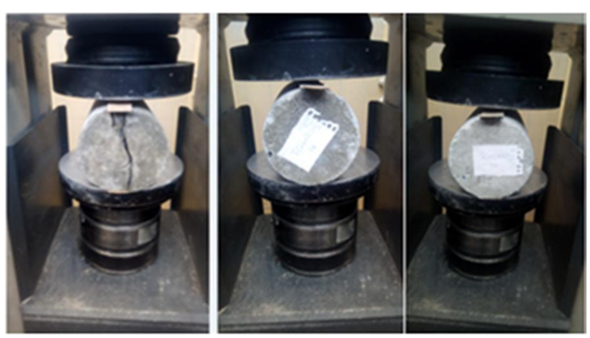
Splitting tensile strength of 7 days cured unmodified concrete showed 4.89 MPa. However, the splitting tensile strength of concrete modified with (0.5 % TNP + 0.2 % WPF) showed 6.02 MPa ,which was 23.11 % modified than unmodified concrete and when compared with the 3 days, it is 1.26 MPa increased or 3.52% increased). The concrete modified with (0.5 % TNP + 0.4 % WPF) showed 7.42 MPa ,which was 51.74 % modification than unmodified concrete and when compared with the 3 days, it is 1.68 MPa, or 7.52 % increased). The concrete modified with (0.5 % TNP) showed 5.73 MPa,which was 17.20 % modified, and when compared with the 3 days, it is 1.15 MPa or 2.13 % increased). The concrete modified with (1 % TNP) showed 5.82 MPa (19.02 % modified, when it compared with the 3 days, it is 0.78MPa or 8.12% increased). Concrete modified with (1.5%TNP) showed 5.78MPa (18.20% modified, when compared with the 3 days, it is 0.81MPa or 6.67% reduced) compared with CCMs. However, the splitting tensile strength slightly reduced from 1%TNP to 1.5 % TNP, which is 0.82 % due to agglomeration effects.

The splitting tensile strength of 28 days cured unmodified concrete showed 5.14MPa. But, the splitting tensile strength of concrete modified with (0.5%TNP + 0.2%WPF) showed 6.18MPa ,which was 20.23% modified than unmodified concrete and, when compared with the 7 days, it is 0.16MPa or 2.88% increased). The concrete modified with (0.5%TNP + 0.4%WPF) showed 9.52MPa,which was 85.21% modified, and when compared with the 7 days, it is 2.1MPa or 33.47% increased). The concrete modified with (0.5%TNP) showed 7.29MPa,41.83% modified, and when it compared with the 7 days, it is 1.56MPa or 24.63% increased). The concrete modified with (1%TNP) showed 7.42MPa, which was 44.36% modified than unmodified concrete and, when compared it with the 7 days, it is 1.6MPa or 25.34% increased), and concrete modified with (1.5%TNP) showed 6.80MPa,which was 32.30% modified, and when compared it with the 7 days, it is 1.02MPa or 14.1% increased). However, the splitting tensile strength slightly reduced from 1%TNP to 1.5%TNP; reduced by 0.62MPa or 12.06% due to agglomeration effects.

The investigation made by (Han, Wang et al. 2017) indicated that, the incorporation of nanomaterials made the concrete microstructures to be denser and, compacted, increased the integrity between the ingredients. On other hand, the cut PET bottles have improved cracking resistance, impact and fracture resistance, since, plastic fibers are flexible, and enable to reduce crack initiation and propagation through the concrete materials.

The incorporation of plastic fibers into the concrete confirmed excellent crack resistant and improved the splitting tensile strength as shown in fig 5.9. The plastic fibers enhanced the adhesion capacity, and bond strengths between aggregates and hydrated cement paste matrix and resulted better splitting tensile strength.

According to the (Bhogayata & Arora, 2018) investigation, plastic fibers have ability to restrict the crack initiation, propagation, and reduced splitting ability of concrete. PET fibers, in concrete mixtures are likely to increase the ductility and toughness, and fracture resistance of concrete materials (Foti 2011).



a b c

Figure 5.9: Testing of splitting tensile resistance of unmodified (a), modified with both TNP & WPF (b), & only TNP modified concrete samples (c)

The above analysis indicated that, the concrete material modified with (0.5 % TNP + 0.4 % WPF) showed extremely greater splitting tensile strength than all the other concrete types. This implies modifying concrete properties with both nanoparticles and fibrous materials showed significant improvement than individual components separately. Modification of concrete with both TNP and WPF combined effects were the most effective method to enhance crack-resistant behavior and ensured durability. The splitting tensile strength of modified and unmodified concrete samples of 3, 7 and 28 days cured concrete and their respective percentages enhanced have been found in table 5.6.

Table 5.6: Splitting tensile strengths of 3, 7 & 28 days of curing

	Split tensile strength, MPa					
Mix Code	3 days	%, enhanced	7 days	%, enhanced	28 days	%, enhanced
CCM	3.98	0	4.89	0	5.14	0
TNP0.5+WPF0.2	4.76	19.6	6.02	23.11	6.18	20.23
TNP0.5+WPF0.4	5.74	44.22	7.42	51.74	9.52	85.21
TNP 0.5	4.58	14.82	5.73	17.18	7.29	41.83
TNP 1	5.06	27.14	5.82	19.02	7.42	44.36
TNP 1.5	4.97	24.87	5.78	18.20	6.80	32.3

The splitting tensile strength of modified and unmodified concrete samples of 3, 7 and 28 days cured has been found in figure 5.10.

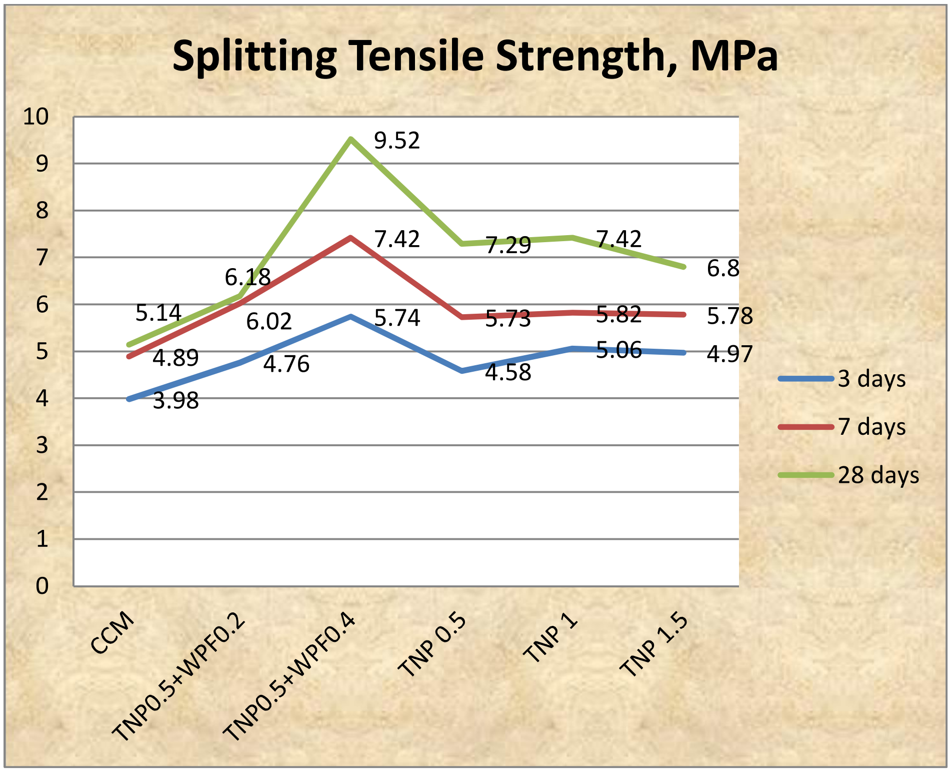


Figure 5.10: Splitting tensile strengths of 3, 7 & 28 days of curing

5.4. Durability Test

5.4.1. Load Resistance of Concrete

The load pressing on the concrete structure is variable, and from time to time it might be changed due to various situations. Therefore, modifying the maximum load resistance capacity of concrete materials is required. In order to develop maximum load resistance capacity, it is very effective method to modify with both TNP and WPF. The reason behind this phenomenon is, due to the filling effects of nanoparticles, and fibers, and forming densified microstructures, and maximized packing density of concrete structure.

The maximum load resistance development of concrete materials of 3, 7 & 28 days of curing has been found in table 5.7.

Table 5.7: Maximum Load resistance capacity of concrete samples of 3, 7 & 28 days of curing

	Load resistance, kN/mm^2					
Mix Code	3 Days	%, enhanced	7 Days	%, enhanced	28 Days	%, enhanced
CCM	0.39	0	0.5	0.0	0.65	0
TNP0.5+WPF0.2	0.53	35.89	0.67	34.0	0.84	29.23
TNP0.5+WPF0.4	0.71	82.05	0.77	54.0	0.87	33.85
TNP 0.5	0.63	61.54	0.67	34.0	0.77	18.46
TNP 1	0.69	76.92	0.71	42.0	0.85	30.77
TNP 1.5	0.63	61.54	0.64	28.0	0.70	7.70

The maximum load resistance capacity of concrete that has been modified with TNP and WPF and unmodified has been shown in the figure 5.8.

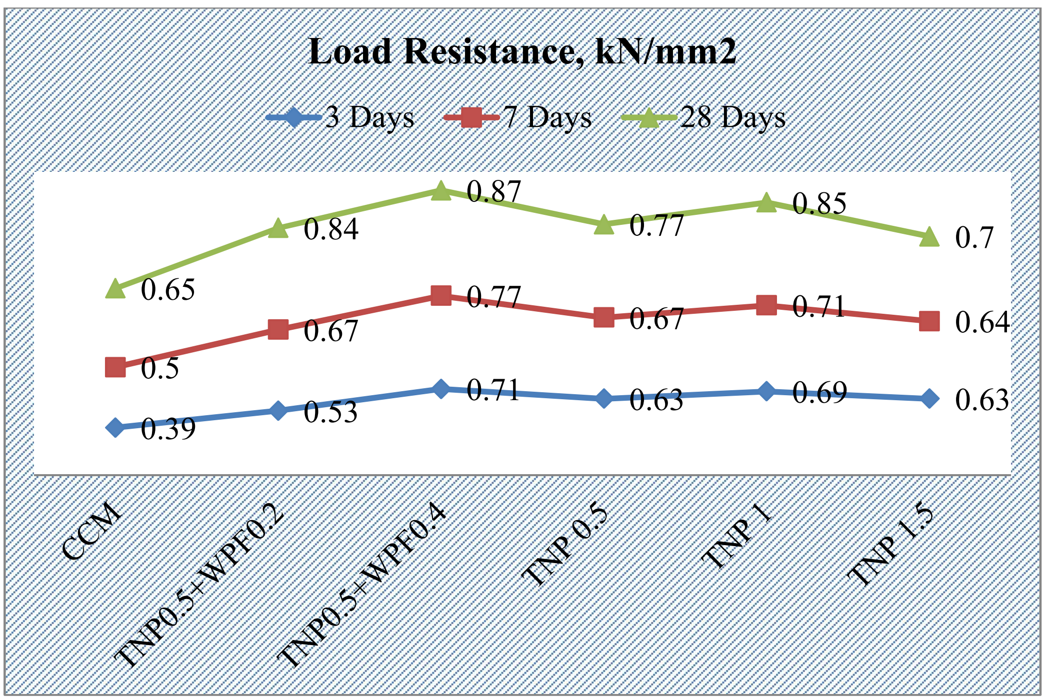


Figure 5.8: Maximum load resistance capacity of concrete samples 3, 7 & 28 days of curing

As the research prepared by (Ceran, Şimşek et al. 2019) revealed, incorporation of smaller amount of TNP form a more compacted and homogeneous structure in the cement. On the other hand, waste plastics fibers have improved toughness and fracture resistance concrete structure.

However, above a certain proportions both nanomaterial and WPF have negative aspects. Nanoparticles became agglomerate or large self-bonding and form a more porous structure, thus losing the positive effect, and the load carrying capacity became reduced.

5.4.2. Water Permeability of Concrete Samples

Water permeability tests can be performed with several methods such as percentage of water absorption, rate of water absorption and coefficient of water absorption. In this thesis, to evaluate the water permeability of the concrete specimens, percentage of water absorption is considered as a criterion of the pore volume or porosity of concrete after hardening, which is occupied by water in saturated state.

The concrete porosity has been reduced due to the filling effects of both TNP & WPF. When, the porosity of concrete materials reduced, and then the water absorption ability became reduced. In addition to the nucleation effects of nanoparticles, WPF blocked the pores and, the water absorption ability became reduced. Especially, due to TiO_2 nanoparticles conversion of extra calcium hydroxide densifies the cement matrix and makes it difficult for water to penetrate. Extraordinary reactivity of nanoparticles also improves the density of the interfacial transition zone between cement paste and aggregate in concrete, which may also mainly lead to lower permeability of concrete. Significantly, lower water absorption was established in the specimens with nanoparticles and WPF, when compared with the control specimens. The high surface area of the nanoparticles and blocking effects of WPF is thought to be main mechanism of these modifications. However, increased contents of nanoparticles becomes agglomerate and can also lead to increased entrapped air voids and reduced strength of cement based materials.

As we can see from table 4.8, the mass loss of unmodified concrete was 134 g. While the concrete modified with (0.5%TNP + 0.2%WPF) showed mass loss of 89 g (reduced by 50.56 %). The concrete modified with (0.5%TNP + 0.4%WPF) showed mass loss of 70 g (91.43 % reduced), concrete modified with (0.5%TNP) showed mass loss reduced to 82gm (63.41% reduced). The concrete modified with (1.0%TNP) showed mass loss of 76 g (76.32% reduced), and modified with (1.5%TNP) showed the weight loss reduced to 88gm (which was 52.27% reduced). The weight loss of concrete after 28 days of curing and their percentages modified has been found in table 5.8.

Table 5.8: Weight loss of concrete samples after 28 days of curing

Mix code	Wt. loss, gm.	%, Enhanced
CCM	134	0
TNP0.5 & WPF0.2	89	50.56
TNP0.5 & WPF0.4	70	91.43
TNP0.5	82	63.41
TNP1	76	76.32
TNP1.5	88	52.27

The combined effects of nanoparticles and waste plastic fiber, have tremendous advantages to decrease the mass loss of concrete materials and, hence enhanced the crack-resistant behavior and improved durability of concrete structure. The fig 5.12 shows, the mass loss of modified and unmodified concrete materials, and their % enhanced.

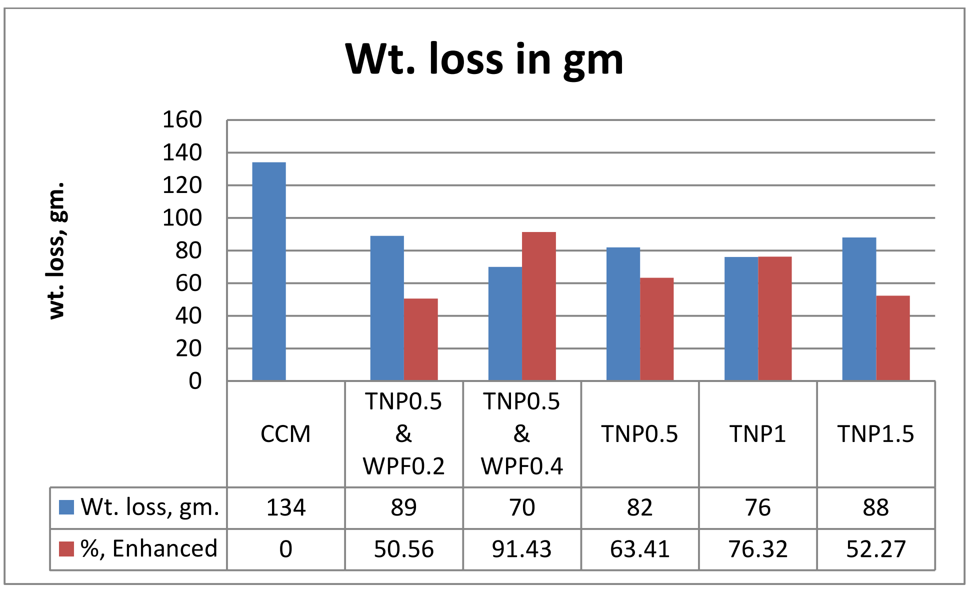


Figure 5.12: Weight loss of concrete samples

The weight loss of CCMs showed the highest value for all the test results. This meant the mass loss of unmodified concrete was dominantly affected by the porosity of the concrete. As shown in figure 5.12, the combined effects of TiO_2 nanoparticles and waste plastic fiber led to an increase of degree of hydration and integrity of concrete.

Results revealed that resistance to weight loss developed due to the positive effects of TNP & WPF on microstructure. Moreover, the lower percentage of mass loss is attributed to the lower permeability of the control sample. Adding nanomaterials as an additive to the concrete mix has affected the hydration reaction & resulted in a lower amount of calcium hydroxide, higher C-S-H gels, and denser structure & reduced porosity. According to (Ceran, Şimşek et al. 2019) investigation, a reduction in the percentage of water absorption may be provided by reducing the total pore volume within a concrete structure.

5.5. SEM analysis

The mechanism in which TiO_2 nanoparticles have improved the concrete microstructure through generating additional components within the concrete structure was examined. The SEM images were shown in fig 5.13 (a, b, and c). The images illustrate the existence of sharp differences in their micrographs in each of the specimens.

Fig 13 (a) shows unmodified concrete, which contains more of unhydrated cement hydration products. The existence of crystals (brighter region) indicated, the formation of calcium hydroxides in the compositions. Thus, these crystalline material make noticeable existence of voids in concrete structure and hence, the microstructure contained cracked regions in its composition. However, lesley a dense rim of hydration product, which is composed of calcium-silicate-hydrate (C-S-H) gels, is seen around cement particles, which is responsible for mechanical strength and durability properties.

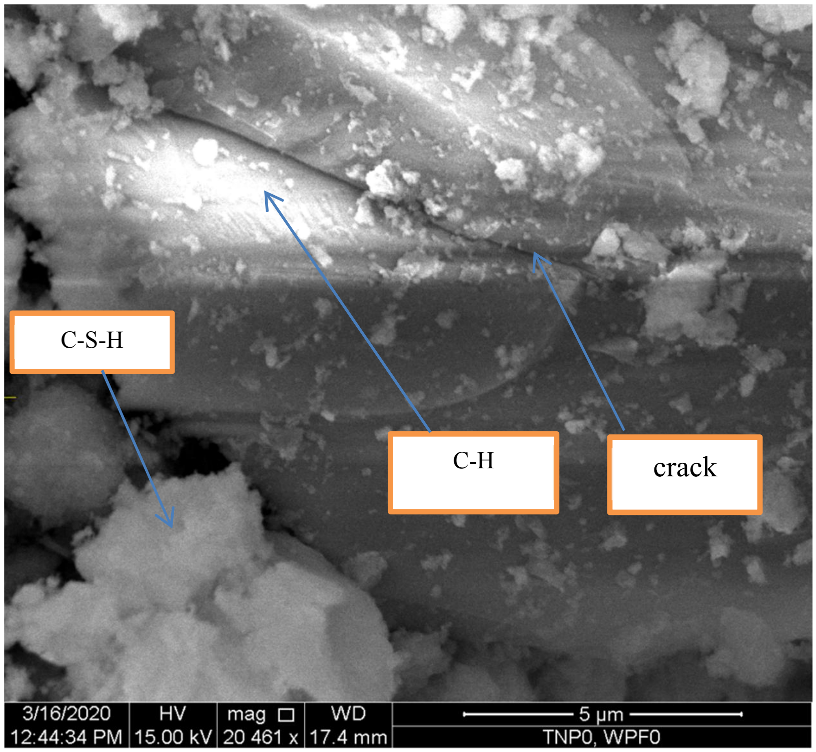


Figure 5.13a: SEM images of 0% TNP & 0% WPF modified concrete

Fig. 5.13 (b) shows (0.5% TNP & 0.4% WPF) modified concrete, where a large amount of gels like materials, which is C-S-H formed. This gel like material is responsible to fill the pores in the concrete microstructure. The concrete material contains 70 wt. % of C-S-H gel like material, in its structure. Uniformly dispersed TiO_2 nanoparticles accelerated the formation of hydration products in the whole concrete structure by controlling the crystallization and hence, restricting the growth of $Ca(OH)_2$ crystals. On the other hand, TiO_2 nanoparticles can act as a filler to enhance the density of concrete, and compacting the microstructure.

Previously conducted study assumed that, the modification mechanisms of nanoparticles on cementitious materials can be divided into three categories. First, the nanoparticles can serve as the nuclei, which will change the hydration process, and thus leading to the morphology change of the hydration products. Secondly, the nanoparticles can fill the nano-sized pores in the amorphous cementitious hydration products to reduce permeability of aggressive agents. Third, the nanoparticles can change the density of C-S-H phase structure & form new high density C-S-H structure. In contrast, both TNP and WPF modified concrete mixture contains many C-S-H gel components and has much fewer voids than unmodified concrete. This is due to the TNP early hydration reaction, which supports to form extra C-S-H gels and improved the microstructure of concrete.

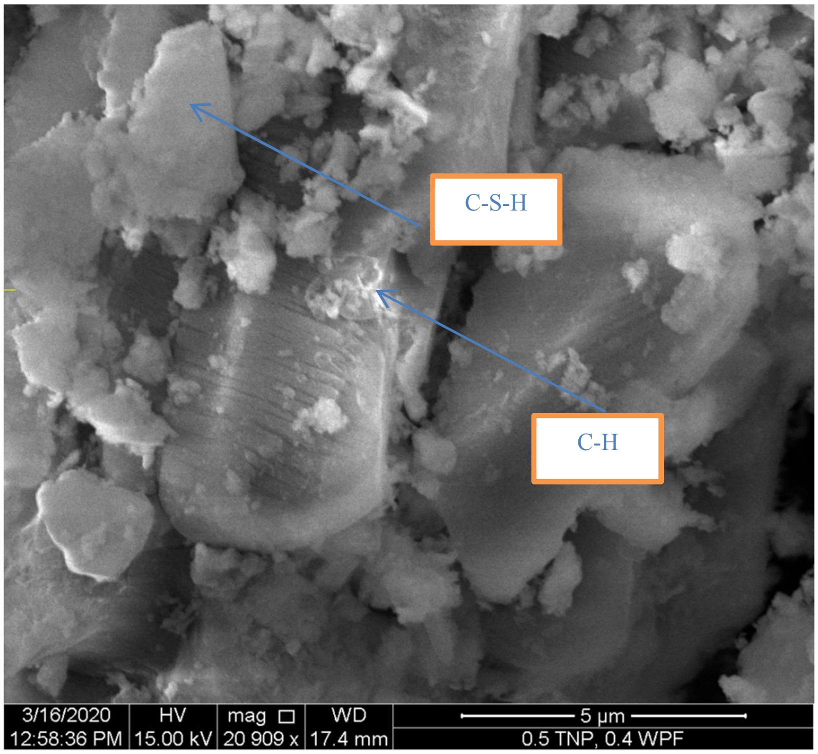


Figure 5.13b: SEM images of 0.5% TNP & 0.4% WPF modified concrete

SEM images of 1% TNP modified concrete was displayed in Fig. 5.13 (c). In 1 % TNP modified concrete, there is excessively large amount of gel like material, which is C-S-H formed. This gel like material is responsible for concrete microstructure improvement. On the other hand, crystallization of concrete components is very limited. The partial substitution of OPC with TNP accelerated the hydration process in concrete and helped to generate more C-S-H gel like material, that in turn, is responsible for enhancing the concrete properties. Therefore, the partial substitution of TNP has improved compactness and densified the structure. This is directly related to modification of strength and durability of concrete material.

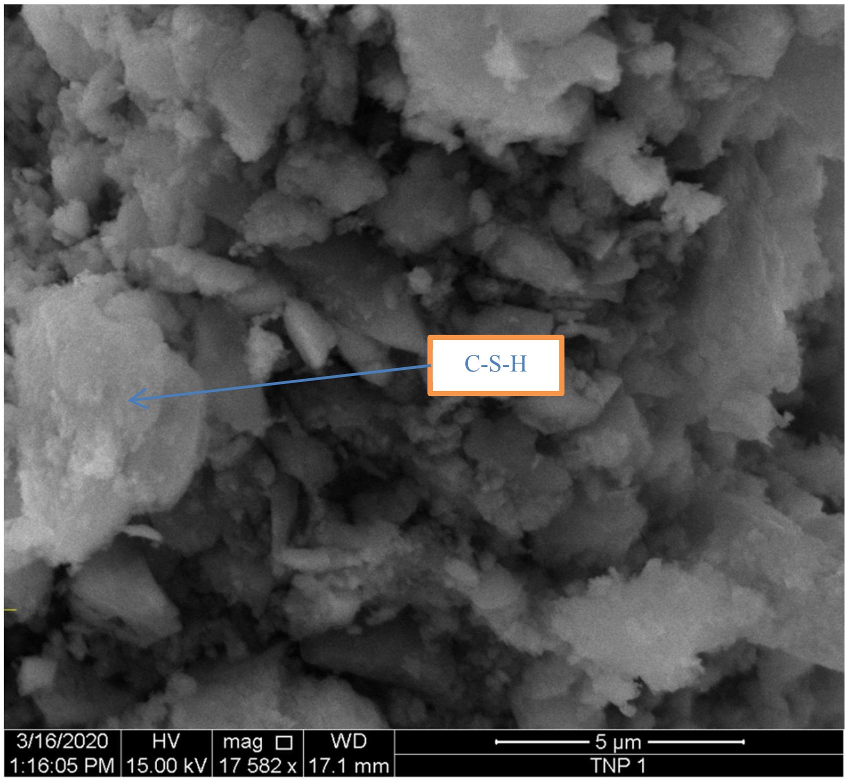


Figure 5.13c: SEM images of 1% TNP modified concrete

According to the investigation of (Harilal et al, 2019), a compacting hydration product, typically C-S-H gel like material have formed in the microstructure of the concrete. The addition of TNP has significant effects the hydration kinetics as well as microstructure of cement paste due to the fact that nanomaterials contribute to the early hydration and more C–S–H gel production (Paul, van Rooyen et al. 2018).

The greater surface area of TiO_2 nanoparticles can accelerate the early hydration reaction in concrete by providing nucleation sites. The review of (Paul, van Rooyen et al. 2018) showed that, the microstructure of concrete can be compacted by using nano TiO_2 and nano SiO_2 particles in the mix. The partial substitution of nano TiO_2 and nano SiO_2 particles increased the formation of C-S-H gel, which can densify the cement matrix and, finally improved the interfacial transition zone between the aggregates and cement paste.

The reaction between these nanoparticles and calcium hydroxide may contribute to the generation of more C-S-H gel and, which fill up the voids and improve the interfacial transition zone and binding paste matrix. However, surplus of nanoparticles can also have a negative effect on the matrix as they may agglomerate and form weak zones (Paul, van Rooyen et al. 2018) .

TiO_2 nanoparticles could be considered as inert, which means it will be hard to react with the cement paste, as a result, it can be inferred that the TiO_2 Nanoparticles will act as seeds, & thus change the growing process & lead to the morphology of the C-S-H phase. The TiO_2 Nanoparticles modified samples shows observable fiber shape hydration product, which is well agreed with the former study (S. XU et al. 2018).

5.6. XRD analysis

The results obtained from XRD tests were analyzed in order to determine the qualitative nature of various crystalline phases in the concrete mix. The XRD patterns of the (0.5 % TNP + 0.4 % WPF), and 1 % TNP) modified and unmodified concrete samples have been shown in fig 5.14.

As the XRD results of CCMs has shown at ($2\Theta = 10.90^o$, 29.44^o, and 29.46^o) unhydrated C-H phases existed, however, which is not existed in (1 % TNP and 0.5 % TNP and 0.4 % WPF) modified concrete. Similarly, in unmodified concrete material, at ($2\Theta = 26.72^o$) and ($2\Theta = 28.76^o$) respectively, unhydrated C_3S and C_2S phases has much intensified than the modified concrete materials. In modified concrete materials, the hydrated C-S-H phases existed at ($2\Theta = 47.14^o$ and 50.26^o), which is not existed in unmodified concrete. In addition to that, the C-H phase in unmodified concrete, at ($2\Theta = 10.90^o$) converted into C-S-H phase in both (0.5 % TNP & 0.4 % WPF) and 1 % TNP modified concrete. In addition, in 1 % TNP modified concrete unexperienced components like, H-C-S (hydrogen calcium silicate) obtained.

In general, the increase in the compositions of C-S-H phases, and simultaneously reduction in the composition of C_3S and C_2S phases is evidence for modification of concrete material. From the diffractogram peaks, it is evident that the peak intensities of portlandite and unhydrated calcium silicates were significantly decreased in modified concrete. This can be attributed due to the facilitation of hydration reaction, and the consumption of $(CaOH)_2$, C_2S and C_3S to form an extra C-S-H gels. Modifiying the concrete material through both TNP & WPF and only TNP used to convert the crystals of $Ca(OH)_2$, C_3S and C_2S into their respective hydrated forms.

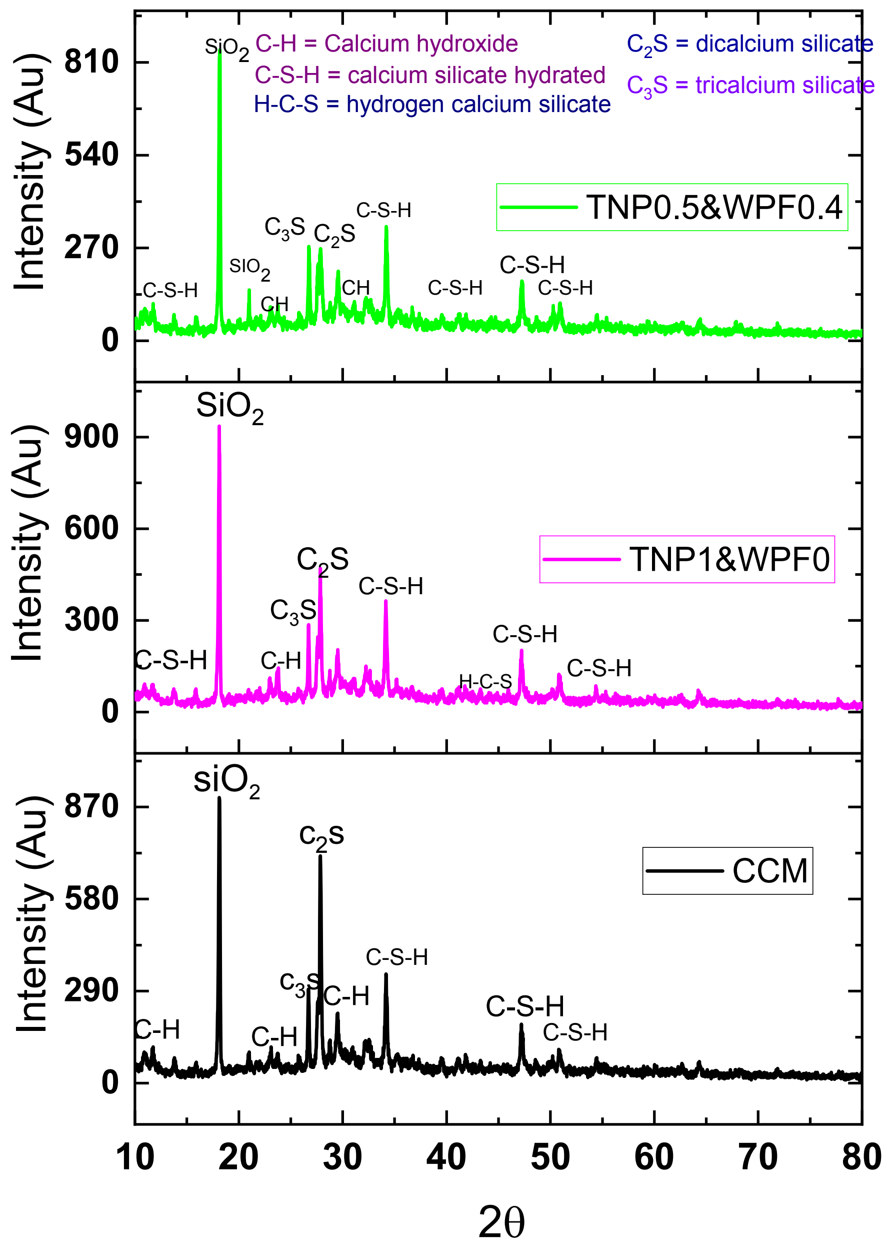


Figure 5.14: XRD results of unmodified, modified with TNP & modified with both TNP & WPF

However, the SiO_2 (quartz) compositions peaks appeared for all the diffractograms at $2\Theta = 18.17^o$, 29.91^o, and 31.18^o and the composition corresponding to quartz has been found to be almost constant in each mix, suggesting the major composition of all mixes is composed of silica due to the highest amount of sand used. The concrete modified with both TNP and WPF indicated the diminishing or disappearing crystalline phases of tricalcium silicates, C_3S (alite) and dicalcium silicates, C_2S (belite) and also portlandites. The existence of more C-S-H phases and loss of alite and belite phases is evidence for modification of concrete containing (0.5 % TNP + 0.4 % WPF and 1 % TNP) modified concrete compared to CCMs.

Therefore, it can be said that increasing of crystalline or amorphous hydrated phases (C-S-H gels) directly contributes to the compressive strength of concrete. Thus, XRD analysis results were in agreement with the modification of compressive and splitting tensile strength of concrete materials, as reported earlier.

5.7. DSC-TGA analysis

DSC-TGA test was conducted on concrete samples prepared from unmodified (0 % TNP + 0 % WPF), and modified with both TNP & WPF (0.5% TNP + 0.4% WPF). TGA test result has shown that the maximum weight loss in CCMs has recorded at reduced temperatures than the modified concrete sample.

It has been observed in the graphs of DSC-TGA, the weight loss of unmodified concrete occurred at reduced temperatures than the modified concrete materials. As shown in fig 5.16 (a), the maximum weight loss of unmodified concrete has recorded at the temperature of 426.43 ^oC, and for modified concrete in figure 5.16 (b), the maximum weight loss has recorded at the temperature of 433.85 ^oC. Very important thing is the weight loss of modified concrete with both TNP & WPF is very less after the maximum weight loss has recorded. But, for unmodified concrete in fig 5.16 (a), in the first stage, the weight loss has located at the temperature of 76.76 ^oC, and it is the result of dehydration of hydrates like C-S-H. Secondly, the maximum weight loss has observed at the temperature of 426.43 ^oC, which corresponds to the dehydroxylation and other hydration products. Thirdly, the weight loss that appeared at the temperature of 667.57 ^oC corresponds to the decarbonation of calcite ($CaCO_3$) in cement paste.

For concrete modified with both TNP & WPF, in the fig 5.16 (b), the first stage weight loss has appeared at the temperature of 82.35 ^oC, which is the result of dehydration of hydrates. Secondly, the maximum weight loss has observed at the temperature of 433.85 ^oC, and which corresponds to the dehydroxylation and other hydration product. Thirdly, the weight loss of concrete appeared at the temperature of 667.57 ^{o}C, and it corresponds to the decarbonation of calcite ($CaCO_3$).

In DSC-TGA graphs, the DSC with the various temperature range was used to measure heat evolution from modified and unmodified concrete. Hence, for unmodified concrete found in fig 5.15 (a), the DSC curve exhibits three main exothermic events during the entire heating process. The first occurs at the temperature from the onset to 105 ^{o}C, but at 106 ^{o}C heat is absorbed; therefore, it is an endothermic transition. From 106 ^{o}C to 340 ^{o}C, crystallization process takes place in the samples, which is an exothermic event, and releases heat, and forms low energy, stable, and ordered structure. The formation of bonds during crystallization is an exothermic process, so an increase in heat flow takes place. Onwards from 340 ^{o}C to 650 ^{o}C, largely crystallization process undergoes. Here, unmodified concrete contains most of crystal-like unhydrated CH, C_2S & C_3S in its structure.

For modified concrete indicated, the decomposition begins late than unmodified concrete as shown in fig 5.15 (b), due to the fact that the materials are more compacted in case of modified. Similarly, the modified concrete exhibits three main exothermic events during the entire heating process. The first exothermic reaction undertakes from the onset temperature to 106 ^{o}C, and heat heat is evolved. But, at 106 ^{o}C, heat is absorbed; therefore, it is an endothermic transition. From 106 ^{o}C to 380 ^{o}C, crystallization process take place again, which is an exothermic event, the concrete material releases heat and forms low energy, stable, and ordered structure. Finally, there is formation of bonds, so an increase in heat flow. Again at temperature of 380 ^{o}C melting process take place. Furthermore, from 380 ^{o}C to 600 ^{o}C crystallization undertakes. Since the concrete modified with (0.5 % TNP & 0.4 % WPF) contains most of C-S-H gels through hydration of CH, C_2S & C_3S, and which is semi-crystalline or amorphous and lower extent of crystallization was observed than unmodified concrete.

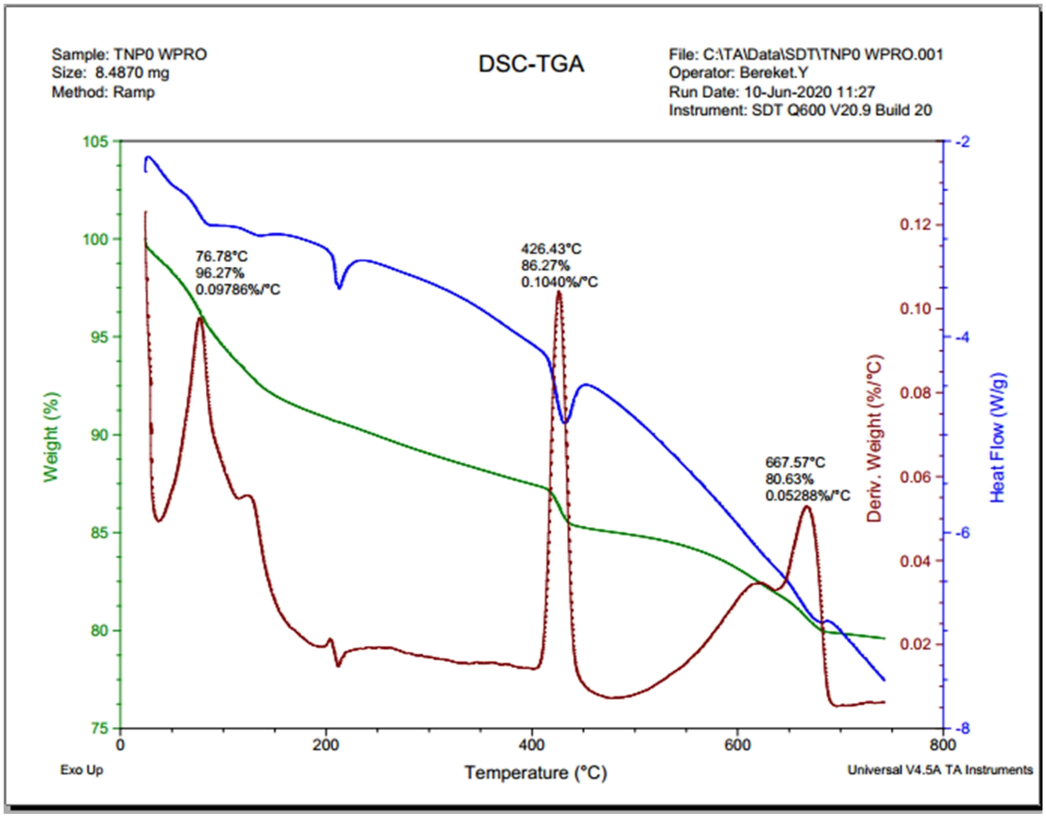


Figure 5.15a: DSC-TGA result of unmodified concrete materials

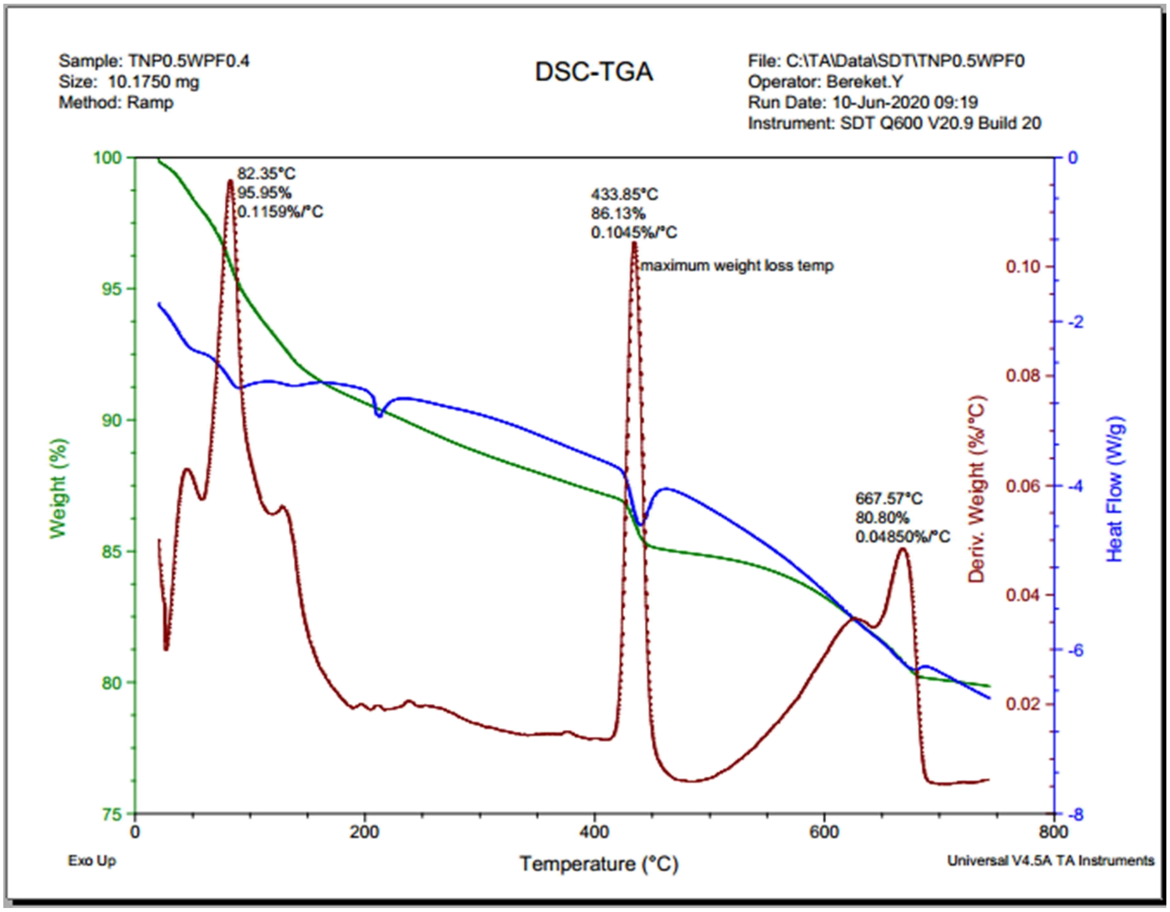


Figure 5.15b: DSC-TGA results of 0.5% TNP & 0.4 % WPF modified concrete

Chapter Six: Conclusions and Recommendation

The results of mechanical strength and durability properties of concrete material modified with both TiO_2 nanoparticles and waste plastics fibers have shown improved properties than unmodified concrete. This was due to the promising features of TiO_2 nanoparticles and waste plastic fibers. All of the modified concrete materials showed enhanced properties with respect to water permeabilitiy, crack resistance behavior, compressive strength and split tensile strength. However, enhancement with both TiO_2 nanoparticles and waste plastic fibers attained was remarkable. For instance, compressive strength of concrete modified with both TiO_2 nanoparticles and waste plastic fibers after 3 days of curing showed increment from 17.3 to 31.57 MPa (82.47 % modification), after 7 days of curing showed from 22.06 to 34.28 MPa (55.39% modification) and after 28 days of curing 29.01 to 39.05 MPa (34.61 % modification). Likewise, split tensile strength after 3 days of curing showed 3.98 to 5.74MPa (44.22 % modification), after 7 days of curing 4.89 to 7.42 MPa (51.74 % modification) and after 28 days of curing 5.14 to 9.52 MPa (85.21 % modification).

As the morphological study indicated for modified concrete, the microstructure becomes compacted than unmodified concrete. Regarding thermal analysis, the weight loss of unmodified concrete appeared at reduced temperatures than modified concrete. The modification was directly related to the generation of additional strength development responsible components, like C-S-H gels in the concrete compositions. This was due to accelerating the cement hydration process at early age. The XRD test of unmodified concrete has shown the existence of various unhydrated phases like CH, C_2S, C_3S and other unhydrated phases and in modified concrete hydrated phases like C-S-H gels.

In general, the concrete materials modified with TiO_2 nanoparticles and waste plastics fiber has clearly shown modification in mechanical strength, durability properties and the whole microstructure too. In this thesis, it is recommended to establish the TiO_2 Nanoparticles manufacturing industry in Ethiopia using locally existing TiO_2 resources for further investigation and full-scale implementation of the finding.

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