



UNIVERSITY OF THE WITWATERSRAND

Development of eco-friendly building bricks derived from carbon nanotube-reinforced coal ash and low-density polyethylene waste materials

By

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degree of

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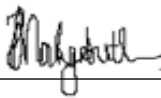
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DECLARATION

I declare that this is my own work, performed under the supervisor of Dr Maubane-Nkadimeng, Prof Coville and Prof Mhlana. This work is being submitted at the University of the Witwatersrand for a degree of Philosophy Doctor. It has not been submitted for another degree qualification.



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31/05/2024

Date

ABSTRACT

This study reports on the incorporation of carbon nanotubes (CNTs) into the all-waste derived building bricks. The focus was on waste management and beneficiation of plastic waste and coal ash, which are generated in large volumes without sufficient recycling. The waste materials were characterized using a range of techniques to ascertain their properties for application. Multiwalled carbon nanotubes (MWCNTs) were synthesized using a facile floating chemical vapour deposition method (CVD) and their physicochemical properties were tested. Bricks with dimensions of 220 x 105 x 70mm were developed with an optimum 85:15 coal ash to plastic waste ratio respectively using a specialized reactor. The bricks were tested for compressive strength, split tensile strength, water absorption, strain, thermal stability and durability using oxygen permeability index, chloride conductivity index and water sorptivity index as indicators. Furthermore, environmental and financial sustainability and ecotoxicology were tested. At optimum conditions, high quality MWCNTs with a diameter of 83 nm, length of 414 μm and a carbon yield of 73% were obtained. The I_D/I_G ratio of 0.44, an oxidation temperature of 649 $^{\circ}\text{C}$, a purity of 94% and surface area of 50.9 m^2/g were achieved. Coal fly ash with a spherical shape, particle size of below 10 micron and a thermal stability of 680 $^{\circ}\text{C}$ was used as an aggregate for the bricks. The bricks (without CNTs) developed their maximum compressive strength of 11.9 MPa at 14 days. The incorporation of the CNTs improved the microstructure of the bricks by filling the voids and providing a bridging effect as reinforcement mechanisms. The optimum CNT loading of 0.05 wt.% produced bricks with a compressive strength of 22 MPa and tensile strength of 8.7 MPa, which exceeded the South African National Standards (SANS227:2007) requirements for building bricks by 450% and 625% respectively. The durability properties were improved as the CNT dosage was increased from 0-10 wt.%. The 0.05 wt.% bricks were categorized as “good” for all the durability indexes. The CNT containing bricks showed improved thermal stability and maintained their structural integrity. The chemical resistance also improved and the efflorescence was minimal on all the bricks. The utilization of waste in the bricks enabled resource conservation, reduced pollution and reduced cost compared to conventional bricks. When only considering the raw materials used, the cost of production per brick was \$0.091. The ecotoxicology of the powdered brick samples was tested on *Raphidocelis subcapitata* (microalga) and *Daphnia magna* (aquatic organism) using leachates from neutral, acidic and basic mediums. Some heavy metals were

leached above the threshold limit especially in acidic medium. The leachates were toxic to the test species at low concentrations and resulted in growth inhibition of the microalga and immobilization of the aquatic organisms. The toxicity of the CNTs was inconclusive and dedicated tests are required to study their effect. With appropriate treatment of CFA, the waste derived CNT bricks have a great potential of being a sustainable alternative to the conventional bricks based on cost, properties and environmental impact.

DEDICATION

I would like to dedicate this work to:

The **Almighty God** who gave me the wisdom and strength to complete this work despite the hardships faced.

My late mother, **Naniky Makgabutlane**: she saw greatness in me way before I could recognise it in myself. She is the reason I pursued this degree. Her love, care, support and prayers carried me through. I am forever grateful for her teachings that contributed in shaping me to be the person I am today. “mama I made it”.

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CONFERENCES

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- 2nd Scale Up Women in Business Summit: SMMES in construction and facilities management 2024
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PUBLICATIONS

- Fungal synthesis of copper nanoparticles and their applications in agri-food, environmental, and biomedical sectors, LN Nthunya, S Mbakop, B Makgabutlane, G Matlou, S Mhlanga, H Richards, *Fungal Cell Factories for Sustainable Nanomaterials Productions and Agricultural Applications*, Elsevier, 91-114 (2023)
- Lab-to-market guide for commercialisation of nanomaterials: A South African university perspective, S Dikweni, B Makgabutlane, SD Mhlanga, *South African Journal of Science*, ISBN: 979-8-218-00238-1 (2023)
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ABBREVIATIONS

ASTM: American Society for Testing Material

BET: Brunauer-Emmett-Teller

CBA: Coal bottom ash

CCI: Chlorine conductivity index

CFA: Coal fly ash

CNTs: Carbon nanotubes

D. magna: Daphnia magna

DI: Durability index

EDS: Energy dispersive X-ray spectroscopy

FFCVD: Floating catalyst chemical vapour deposition

FTIR: Fourier-transform infrared spectroscopy

HNO₃: Nitric acid

LDPE: low density polyethylene

LOI: Loss on ignition

MWCNTs: Multiwalled carbon nanotubes

NaOH: Sodium hydroxide

OPC: Ordinary Portland Cement

OPI: Oxygen permeability index

R. subcapitata: Raphidocelis subcapitata

SANS: South African national standards

SEM: scanning electron microscopy

TGA: Thermal gravimetric analyzer

TEM: Transmission electron microscopy

WSI: Water sorptivity index

XRD: X-ray diffraction

CHAPTER 1

1. Introduction

1.1 Background of the study

The large volumes of waste (e.g., paper, plastics, rubble, coal fly ash (CFA), coal bottom ash (CBA)) generated by growing industries and increasing human activities puts pressure on the waste management systems [1]. Unfortunately, not all industries or people can depend on the local municipalities for a solution to the waste collection and management issues. This ends up leading to the generation of unauthorized dumping sites that pose both environmental and health risks. The accurate cost of waste not only involves the cost of thrown away materials, but includes ineffective utilization of raw materials, futile usage of water and energy, destruction of excess products, disposal of by-products, waste collection and treatment, as well as wasted labour [2]. The cost of waste disposal is always on the rise and also recycling incentives are provided to encourage the repurposing of the waste for other applications. For example, in recent years the cost of plastic bags in South Africa increased drastically to encourage consumers to reuse their bags or choose sustainable alternative [3]. However, “reuse” is a lesser preferred measure, as is disposal, as they are reactive approaches rather than preventative approaches to waste issues (see Figure 1.1) [4]. One method to achieve this aim is to replace the use of plastics with more sustainable materials (i.e., cellulose from biomass) as a preventative measure [5]. Furthermore, greener energy generation methods (i.e. hydro, solar and wind) are on the rise as alternatives to substitute coal powered energy processes which produce high amounts of waste (i.e. carbon dioxide and coal ash).

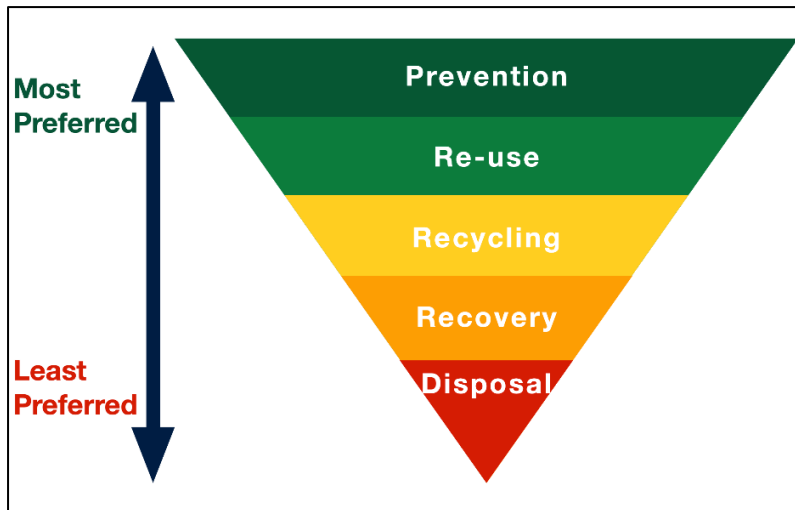


Figure 1.1: Waste management hierarchy [4]

It is still a long journey to reduce the generation of waste. However, its production should be minimized and managed effectively. There are many types of waste and can be categorized in various ways for effective recycling as shown in Figure 1.2. The focus of this study is on solid waste i.e., coal fly ash, coal bottom ash and plastic waste (low density polyethylene) and its re-use.

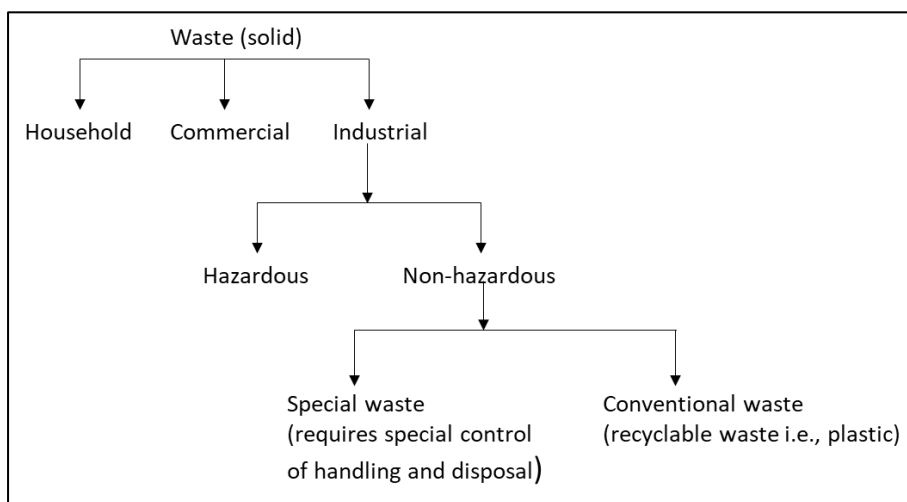


Figure 1.2: Classification of solid waste

1.1.1 Plastics

Plastics are a significant part of our everyday lives owing to their versatility in application. Industries use plastics for many applications that include packaging of food items and

electronics to the manufacturing of plastic-based products such as chairs, toys, pipes, automobile parts etc. [7]. One of the most widely used plastics in households are plastic bags to carry groceries and clothing; they can be reused, for example to carry garbage for disposal purposes [8].

Plastics have a greater global market due to lower processing costs, durability, strength and chemical resistance [9]. However, these excellent stability properties of plastic also create an environmental threat and is detrimental to the ecosystem. These plastics are chemically non-biodegradable, making their disposal a major concern. This is due to the fact that plastic waste lasts a long time—natural decomposition can take up to 500 years [10]. The thermoplastic waste, which is primarily composed of poly-olefins, comprises over 32% of low-density polyethylene (LDPE) and accounts for over 78% of the total plastic waste produced annually [10]. This waste is generally placed in land fill sites. The plastic can persist in the form of microplastics, finding its way into the ground water, tap water, river banks and ultimately the sea [11]. Plastics are the largest contributor to aquatic life harm and have also become a health risk to human life [11].

Recycling of plastics can reduce their negative environmental impact. Researchers have focused on various recycling and reutilization strategies to transform plastic waste to generate oil/gas products and energy [12,13], to produce carbon precursors applicable in the synthesis of carbon nanotubes (CNTs) [14] etc. In order to create products with high compressive and flexural strength and mechanical resistance comparable to typical concrete products, the plastic waste can also be turned into aggregates for concrete mixtures [15]. It is well known that plastic has a high linear burning rate and is highly flammable [16]. Fillers are therefore needed to enhance its mechanical and physical qualities and lessen its flammability.

1.1.2 Coal fly ash and coal bottom ash (coal ash)

Coal ash is another type of noxious combustion-waste, produced in large quantities by thermal power plants. The waste is especially a challenge in a developing economy like South Africa that heavily relies on coal combustion for energy generation due to the high availability

of coal. The power utility, (ESKOM, in South Africa) reported in 2018 that it generates 34.4 Mt of coal fly ash annually. Currently, only 2.41 Mt is beneficiated while the rest is unutilized and stored in ponds, landfills and ash dams [17]. The coal powered energy generation value chain which involves coal mining, transportation, preparation, combustion and by-product storage results in numerous unsustainable environmental impacts [17]. Furthermore, the CFA and CBA both contribute to air contamination and can be considered health hazards. They consist of fine particles (0.5-400 μm) that can simply infiltrate the air passages and cause breathing problems [18].

Research towards the use of CBA has been slower compared to that of CFA. The reasons are that it makes up considerably less than CFA, at just 25% of the total amount of coal ash generated [19]. Additionally, it has been shown that CFA is the more dangerous industrial waste, whereas CBA is said to have fewer toxic elements. Lastly, CBA is inhomogeneous, which makes it harder to recycle and limits its applicability [19].

Although CFA and CBA are both regarded as a waste product, they have been studied as aggregate materials for various applications. They have valuable properties such as being light weight, easy availability, low density, chemical inertness and thermal stability [20]. The largest application of CBA is as an aggregate in construction composites because its particle size distribution is similar to that of sand [21]. The largest consumers of CFA are the cement industry, utilizing more than 40% of the fly ash produced annually worldwide [22]. However, a specific grade of coal ash, with low loss on ignition (LOI), is required for application in construction, thus leaving the unrequired grades in ash dumps [23].

The residual carbon in coal ash can absorb water and chemical admixtures (such as superplasticizers and air-entraining agents) in cement composites, decreasing their effectiveness or perhaps leading to an insufficient air-void system in the concrete. The pozzolanic reaction is inhibited by the lower fineness brought on by the coarser carbon particles [26]. Thus, it is commonly anticipated that low-quality coal ash with a high LOI and low fineness may hinder the development of concrete's strength [27]. Due to their ceramic-like properties, ash-based composites generally exhibit quasi-brittle behaviour together with poor tensile strength and fracture toughness [28].

The limitation of the current studies with the use of waste in building bricks is their low inclusion due to the properties of the bricks being compromised at higher waste dosages. Coal ash is usually used as a partial replacement of cement/ clay in bricks and it is mostly applied in concentrations of up to 40 wt.% [29]. This is because cement/clay are the primary strength developing aggregates used in conventional bricks and their reduction affects the mechanical properties. In a recent study, Islam et al., found that higher amount of CFA (20% and 25%) replacement showed lower compressive strength of the bricks at 28 and 90 days. This was attributed to the increase in silica (contained in CFA) and the gradual reduction of calcium oxide (contained in OPC) in the concrete, leading to unavailability of CaO for pozzolanic reaction. Furthermore, it was found that the workability of fresh concrete reduced when the inclusion of CFA exceeded 10% of the cement [30]. Siddique, used higher loadings of CFA and observed that the inclusion of 35%, 45%, and 55% CFA as a replacement for cement resulted in reductions of 23%, 36%, and 49% in the split tensile strengths of concrete bricks, respectively [31]. Other researchers found that the flexural strength of 10%, 20%, 30% and 40% CFA concrete decreased by 5.26%, 7.89%, 10.53% and 21.05% respectively, compared to the control at 28 days [32].

Plastic waste is currently used as a partial replacement of fine and coarse aggregates such as sand and stones at dosages of up to 40 wt.% [33]. Vanitha et al., used plastic waste to partially (0-10 wt.%) replace coarse aggregates in concrete blocks. It was found that above 4 wt.% inclusion, the compressive strength decreased by 9% [34]. Osei et al., found that the use of plastic aggregate in structural concrete at dosages higher than 36% was not suitable as it reduced the compressive strength. The only desired property obtained by the higher dosages of plastic waste was lighter composites [35]. Jaivignesh et al., replaced fine and coarse aggregates in concrete with 10%, 15% and 20 % plastic waste and also added steel fibers to counter the impact of plastic on the compressive strength. The composites still suffered a reduction in compressive strength and as such it was concluded to use plastic waste as a green aggregate despite its impact on the compressive strength [36].

The use of coal ash as a 100% replacement of conventional strength developing aggregates such as cement and clay is novel to this study. The coal ash is solely used as an aggregate and does not impart its pozzolanic properties which are known to facilitate the hydration reaction

and strength development due to the absence of water. Furthermore, plastic waste was used as a binder (liquified), unlike it is conventionally used (shredded solid particles) as a partial replacement of fine and coarse aggregates. The use of CNTs as a reinforcement filler in the all-waste derived bricks is unique to the study. The CNTs are incorporated to counter the negative impact of the waste materials on the properties of the bricks as previously reported in literature.

Recent studies have focused on the use of nanomaterials for composite reinforcement, including graphene-based materials, nanosilica, nanotitanium dioxide (TiO₂), and CNTs [37-39]. CNTs have a high surface area and high aspect ratio in addition to having exceptional mechanical, electrical, thermal, and optical properties [40]. With a tensile strength of 150 GPa, which is 100 times higher than steel [41], CNTs are lightweight materials that greatly enhance the mechanical properties of composites. The filler-effect caused by their nanosize and hydration chemistry improves the behaviour of coal ash binders both fresh and hardened, as well as reducing shrinkage-related micro and macrocracks [42]. The mechanical properties of cement are significantly improved by the inclusion of small amounts of multi-walled CNTs (MWCNTs), between 0.05 wt.% and 0.5 wt.% [43]. When CNTs are added to concrete, it is anticipated that the compression strength would rise to 200 MPa, enabling the building of skyscrapers that reach mile-high heights [42].

The disposal of plastic and coal ash (CFA and CBA) is unsustainable and is too costly to manage; it is already forbidden in certain countries [44,45]. Thus, alternative applications are required for the utilization of these waste materials. In this study, a green sustainable approach was developed to utilize waste materials (plastic and coal ash) for the manufacturing of CNT reinforced bricks. This encourages a closed resource loop by transforming waste to high value products.

1.1 Motivation of the study (Problem Statement)

Plastic waste is the largest contributor of global solid waste [46]. This is due to its high production rate for application in many industries. However, plastic reuse and recycling processes remain a challenge since the waste is not adequately categorized for further

processing. Another waste generated in large quantities is coal ash (CFA and CBA) [47]. This waste has limited applications compared to the rate of its production.

The application of plastic waste to produce materials for building is a conceived and tested idea [48-50]. Although this has also been achieved using coal ash, the process often involves the use of other materials such as cement. Also, the use of coal ash for making bricks using the standard processes is limited by water scarcity, as the process involves the usage of high volumes of water [51]. Furthermore, the application of waste materials in bricks has been shown to compromise their properties; as such it is added in limited amounts to maintain the desired properties that are acceptable for building bricks. This restriction further reduces the amount of waste that is recycled. Thus, alternative ways of making useful products from coal ash and plastic waste are desired.

Our approach was the novel simultaneous incorporation of CNTs, coal ash and plastic waste to develop bricks. Due to their excellent properties, CNTs provide strength, binding capacity and thermal stability to the final product. The incorporation of the CNTs in the bricks ensures that higher volumes of waste are used in the bricks without compromising their properties. This is due to the superior properties they impart as a reinforcement to the bricks. The synthesis of these bricks does not require cement and thus, no water was used during production. This approach also reduced pollution while creating useful products from waste that are generally not used in the conventional synthesis of concrete mixtures and bricks. Moreover, the bricks were eco-friendly, sustainable and low-cost as the method used waste materials and greener processes. Ultimately the successful use of such nano-enhanced bricks will potentially lead to the creation of new products, jobs while solving environmental waste problems.

1.2 Purpose of the study

1.2.1 Research questions

The study sought to answer the following research questions.

- Will the waste materials be suitable to develop the eco-friendly bricks?

- What concentration of CNTs will be required to reinforce the composite for their application as building materials?
- Will surface treatment of CNTs significantly improve their dispersion in the composite?
- Will the CNTs and coal ash improve the thermal stability of the composites? If not, what modification will be done?
- Will CNTs significantly improve water resistance and durability of the composites?
- Will the composite materials be strong enough (mechanical strength) for structural application in building and construction?
- Will the developed bricks be more environmentally and financially sustainable compared to the conventional bricks?

1.2.2 Aim of the study

The aim of the study is to develop building and construction eco-friendly bricks derived from CNT-reinforced waste materials (plastic and coal ash).

1.2.3 Objectives

- To collect, classify, pre-treat and characterize CFA, CBA and plastic waste materials (LDPE) using a range of techniques.
- To functionalize and characterize the synthesized CNTs in order to increase their dispersion in the bricks.
- To study the physicochemical properties of the bricks developed from different raw materials and the effect of the inclusion of CNTs. Furthermore, test their applicability according to the building and construction standards.
- To study the durability properties of the developed bricks.
- To assess the environmental impact and financial sustainability of the developed bricks as compared to the conventional bricks.

1.2.4 Hypothesis of the study

The expected properties of the engineered building bricks are summarized:

- High strength desired for building. The bricks can be made stronger than concrete bricks but not too strong to prevent them from being cut and chiseled with the usual tools.
- The bricks should possess hydrophobic properties as a result of the incorporated CNTs. This means they should not absorb excess water into their internal structure. Thus, possess high durability.
- The bricks must be thermally stable to withstand high temperatures desired for buildings.

The proposition of this study is that the CNT-reinforced bricks will have a great potential with comparable and even improved properties relative to conventional concrete/ clay bricks.

1.3 Thesis layout

This thesis does not have a dedicated methodology chapter, but rather details the methods and procedures undertaken in each chapter.

Chapter 1 gives a background, motivation, aim and objectives of the study.

Chapter 2 presents a detailed literature review of the work that has been done and highlights the identified gaps that are bridged by the study. This chapter has been published: *B Makgabutlane, M Maubane-Nkadimeng, N Coville and S Mhlanga, 'Plastic-fly ash waste composites reinforced with carbon nanotubes for sustainable building and construction composites: A review', Results in Chemistry, 2022, 4, 100405.*

Chapter 3 details the synthesis of carbon nanotubes using a facile approach of a floating catalyst vapour deposition. Parts of this work were published in a conference proceeding: *B Makgabutlane, M Maubane-Nkadimeng, N Coville and S Mhlanga, 'Facile floating catalyst chemical vapour deposition synthesis of multiwalled carbon nanotubes for application in sustainable construction,' TechConnect Briefs. 2022, ISBN: 979-8-218-00238-1.*

Chapter 4 reports on the characterization of all the raw materials (coal fly ash, coal bottom ash and low-density polyethylene) used in this study.

Chapter 5 presents the application of carbon nanotubes as a reinforcement filler in the waste derived bricks.

Chapter 6 outlines the durability of the bricks under various conditions.

Chapter 7 focuses on the environmental and economical sustainability of the bricks.

Chapter 8 concludes the study and gives recommendation on the future prospects.

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CHAPTER 2

PLASTIC-FLY ASH WASTE COMPOSITES REINFORCED WITH CARBON NANOTUBES FOR SUSTAINABLE BUILDING AND CONSTRUCTION APPLICATIONS: A REVIEW

2. Introduction

Bricks are a large and important part of the building and construction industry and have been used as masonry units due to the strength and durability they provide in structural applications [1]. The properties of each brick produced depend on the raw materials used and their preparation methods [2]. The commonly used bricks are those produced from clay, cement concrete and recently fly ash, with clay bricks being the most ancient and widely used [3]. Clay is made up of alumina and silica, with the latter being the promoter of particle fusion at low temperatures and determines the colour of the brick produced [4]. A typical brick manufacturing process involves: i) raw material preparation and mixing, ii) brick formation, iii) drying, iv) firing and v) cooling [4]. Clay bricks are either burnt (fired) or unburnt (unfired) during the production process. Burnt clay bricks obtain their strength through the sintering process, where the crystalline mineralogical phases in clay are fused into the pores to strengthen the microstructure of the brick. Their mechanical and durability properties are also dependent on the type of clay, water ratio, burning and curing process [5]. Unburnt clay bricks are normally incorporated with lime stabilizers to foster the pozzolanic reaction, which ensures effective particle bonding and thus aids the stiffness and mechanical strength in the bricks [6]. Furthermore, the size and geometry of the bricks have an effect on the mechanical performance of wall panels [7].

Concrete bricks are another type of conventional brick made of Ordinary Portland Cement (OPC), water, aggregates and additives [8]. Aggregates in concrete bricks comprise of 65-70% of the total volume of a brick [9]. Thus, the construction industry is considered to be among the largest consumer of natural resources. The process of cement production is an energy intensive one using about 4 GJ energy per ton of cement produced [10]. Furthermore, 622 kg of CO₂ per ton of cement is produced as well as other hazardous greenhouse gases during fuel combustion and limestone-calcination [10]. Similarly, clay bricks use great amounts of natural resources which causes ecological degradation due to excessive movement/removal

of the brick constituent from the environment. The firing process to make burnt clay is normally performed at temperatures between 1000-1200 °C and can take up to 5 days [11]. This process is almost 300% more energy demanding as compared to the manufacturing of concrete bricks [10].

It is evident that the conventional brick production methods are not environmentally benign as they contribute a great deal to carbon emissions and are also not economically sustainable. The building and construction industry is the backbone of the economy for many countries, and as such, alternative ways of producing bricks in the future that are eco-friendly and affordable is crucial. This is also important in addressing the sustainable development goals (SDGs), such as SDG 13 of climate action; which has an agenda of reaching net zero carbon by 2050 [12]. Furthermore, sustainable building materials speaks to SDG 9 & 11 of industry innovation and infrastructure and sustainable cities and communities respectively [12]. The application of sustainable building materials has a positive impact on both the quality of people's lives and the environment.

The incorporation of waste into bricks as sustainable construction materials is among the studies that have gained considerable attention. This is due to rapid industrialization that results in the production of large volumes of waste which causes disposal and handling problems. Moreover, significant volumes of construction materials are necessary for the creation of infrastructure, such as used in buildings for housing and industries as well as facilities water and sewage storage [13]. Thus, sustainable approaches are required to meet this ever-growing demand. Zero-cement products known as alkali-activated bricks have been developed as sustainable construction materials [14]. These products utilize waste such as rice husk, fly ash, bottom ash, cement kiln dust, blast furnace slag and mine tailings [15–17]. These bricks are produced by alkali activation (sodium hydroxide (NaOH) or potassium hydroxide (KOH)) of the aluminosilicate source material. Alkali-activated bricks are developed through a process of geopolymerization. The process relies on the particle size, loss on ignition and the alumina-silica content of the source materials [18]. The process results in creation of high strength eco-friendly products with a compressive strength between 5-60 MPa and a density of 1400-1500 kg/m³ [19]. For example, Gavali et al., produced alkali activated bricks using co-fired blended ash and stone with a compressive strength of 5–15 MPa, water absorption of 6–14% and thermal conductivity of 0.35–0.40 W/(m.K) [17].

Similarly, in another study Gavali et al., used the same industrial waste to make sustainable bricks. The alkali activated bricks resulted in bricks with a reduced cost (7%), embodied energy (22%) and lower operation energy (13%) compared to bricks used in conventional buildings [20].

Reusing construction concrete waste materials (i.e. ceramics, bricks, blocks, pillars) as pozzolanic admixtures in the production of new products is another sustainable approach to minimize the depletion of natural aggregates, reduce energy usage and environmental pollution. These waste materials mainly come from demolitions, renovations and products with defects. They effectively substitute or even replace cement and aggregates in construction materials [21]. The waste is crushed and used as either small or large aggregates. The replacement ratio is normally between 1- 50 wt.% of cement or aggregates [21]. Gencel et al., replaced clay with up to 15 wt.% concrete waste and obtained a compressive strength of about 7 MPa, which met the required standard [22]. There are other waste materials that have been incorporated into bricks to reduce the reliance on non-renewable resources. These include paper processing residues, cigarette butts, textile sludge, mill scale, marble slurry, polystyrene foam, straw, polystyrene fabric, cotton waste, dried sludge, rubber, wood sawdust and waste plastic [23,24].

When hybrid composites, consisting of reinforcement and matrix materials are made, the former impart their distinct mechanical and physical properties to the brick to enhance the matrix properties [25]. The incorporation of waste materials in construction composites can compromise some of the brick properties. For example, plastic waste is known to have a high linear burning rate which renders it flammable [26]. Its incorporation in construction materials compromises the thermal stability of the product, which is a set standard requirement.

This review seeks to evaluate the application of waste materials, in particular, coal fly ash and plastics, their typical replacement ratios and their physicochemical properties, in construction composites (bricks). The influence of nanomaterials, especially CNTs, as a reinforcement filler in the brick composite made of waste, is also described. As will be seen, the success of hybrid composites is based on strong linkages between the individual materials to ensure the nanomaterials do not agglomerate in the composite and actually facilitates load transfer. Thus, a mechanism is proposed with the aim of understanding the interaction of waste

materials and CNTs within the composite. Lastly, the potential release of CNTs to the environment is review. This is to ensure safe usage of CNTs from application to end of life cycle of its products.

2.1 Application of waste materials in construction composites

The generation of high volumes of waste is both an environmental and economic challenge. It has become unsustainable to manage this waste. Thus, recycling of waste into valuable products has become part of the sustainable development goals for many countries. Plastic waste and coal fly ash are among the largest contributors of solid waste generated by the plastics (polymers) and mining industries respectively [27]. The rate at which these waste materials are generated requires large industrial applications, such as in the building and construction industries, to utilize them. The application of plastic waste and coal fly ash in construction composites is reviewed below.

2.1.1 Waste Plastics

Plastics are among the largest contributors of the total global solid waste generated, with low-density polyethylene (LDPE) being the most produced [28] (Figure 2.1). LDPE plastics mainly include household items such as plastic bags, squeezable plastic bottles, frozen food containers, and cosmetic and detergent bottles [24]. These items are generally used once and discarded, typically in disposal sites. They also later find their way into the ground water, riverbanks and ultimately the sea. South Africa ranks as the 11th country (out of 192 countries) with the highest level of mismanaged plastic waste entering the ocean [29]. Plastic waste pollution in the costal environment has an adverse effect on aquatic life and poses a health risk to humans [30]. Thus, recycling and reusing plastic is a sustainable solution for reducing the negative impact the waste has on both the environment and the quality of life. The recyclability of plastics is dependent on their type and properties. Plastics are categorized as either thermosets or thermoplastics according to their characteristic properties [31]. Thermoset plastics have polymers that combine to form irreversible chemical bonds during

curing process. Their strength is reinforced when heated, however, following the heating they cannot be reshaped or reheated [32]. Thermoplastics are the most common type of plastic and are easier to recycle and reuse due to their ability to be molded and remolded. Current thermoplastics soften in the range of 65°C-200°C [33]. The prominent characteristics of typical thermoplastics are shown in Table 2.1. These properties inform their suitability in application and their recyclability. Polyethylene terephthalate (PET) has the highest melting point and would thus require higher energy to recycle compared to the other types of plastics.

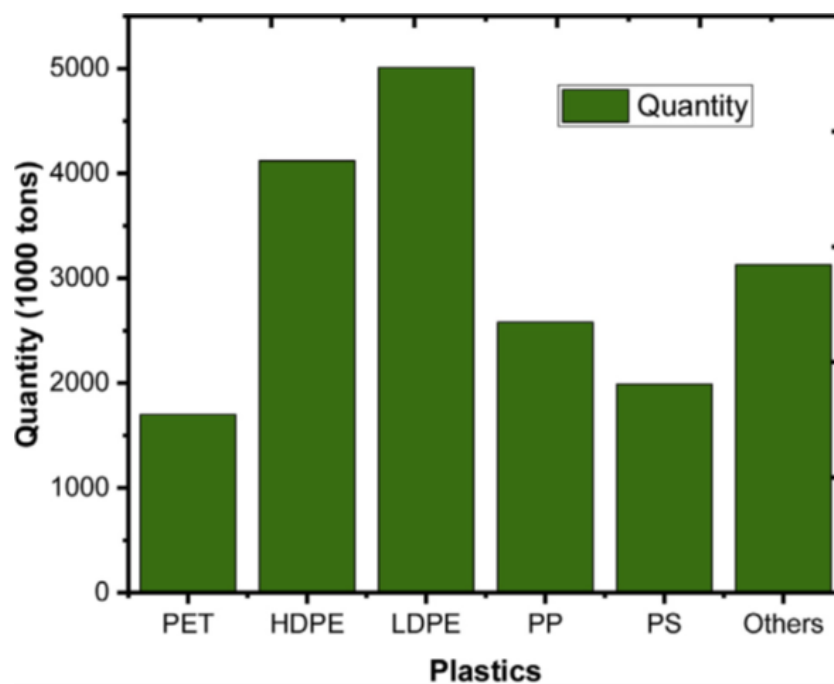


Figure 2.1: Estimated quantities of waste plastic generated in a year (PET= polyethylene terephthalate, HDPE= high density polyethylene, LDPE= low density polyethylene, PP= polypropylene, PS= polystyrene) [34]

Table 2.1: Properties of different plastics commonly found as waste in the environment [35]

Properties of plastics	Types of plastics				
	Low-density polyethylene	High-density polyethylene	Linear low-density polyethylene	Polypropylene	Polyethylene terephthalate
Density (g/cm ³)	0.92	0.94-0.96	0.92	0.905	1.37
Melting point (°C)	105-111	126-135	130	160	225

Max service temperature (°C)	80	80	50	80	70
Tensile strength (MPa)	0.2-0.4	0.2-0.4	0.2-0.4	0.95-1.3	0.25
Notched impact strength (kJ/m ²)	No break	No break	No break	3-30	1.5-3.5

The application of plastics is vast due to their inherent characteristics such as high impact resistance, their light weight and flexibility to be molded into different shapes. They are also resistant to bacteria [34]. However, they are not biodegradable. Notably, there are benefits to incorporating plastic waste in construction materials (Figure 2.2). According to Figure 2.2, the usability lifespan of plastics is shorter than its non-usability life span and thus, the plastic persists for years as unusable waste rather than as a valuable product. Similar to coal fly ash, it is a waste by-product which persist longer as waste than a valuable product due to its limited applications. In contrast, concrete has a longer usable lifespan than its non-usable lifespan [36]. Therefore, the insertion of waste such as plastic and fly ash in concrete materials is a sustainable approach for recycling and safely disposing waste products. Importantly, the limitations of labour intensive sorting, which is a strict requirement in other industries, is exempted in some construction applications [27]. This makes the recycling process easier and less costly. Furthermore, the utilization of waste in construction materials not only reduces pollution but also the number of natural aggregates used, which are responsible for environmental degradation and the depletion of natural resources.

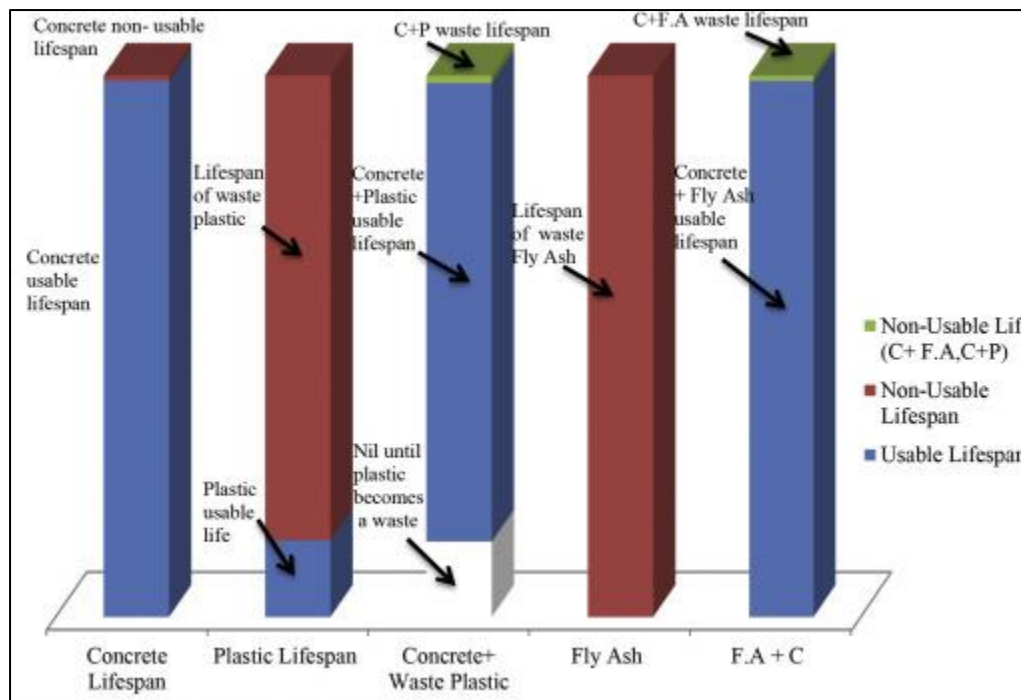


Figure 2.2: The benefits of using waste in concrete, C= concrete, FA= fly ash, P= plastic [36]

2.1.1.1 Processing plastics for application in construction composites

Like any composite material, the controlling factor towards the successful application of the composite is the interfacial transition zone between different materials. The substitution of natural aggregates such as sand with plastic reduces the density and compressive strength of a composite at high substitution ratios, resulting in a loss of strength [37]. This may be as a result of the hydrophobic surface of the plastic leading to excess water, thus, increasing voids and also of poor bonding between the plastic and the matrix. Appropriate mix design as well as the choice of the type of plastic waste can limit the reduction of strength [8]. Furthermore, reduction in compressive strength can be minimized by improving the chemical and physical bonding in the concrete mix. Different physical and chemical approaches exist to achieve this in construction mixtures.

Physical approaches, such as shredding plastic to smaller particle sizes is normally the first treatment step. During shredding, the size of the plastic is reduced to a range of 2.36 mm-4.75 mm. This process has been shown to improve blending in concrete mixes and to minimize the loss of compressive strength [38]. Tulashie et al., used shredder blades to obtain 3 mm plastic waste. The shredded plastic, together with the pit sand or sea sand, were placed

in an extrusion machine in batches. The batches were melted at 175 °C until there were no longer flakes [38]. In another study, LDPE was grinded after being melted at 120 °C into a semi-liquid form using a pestle and mortar. Then a 4.75 mm sieve was used to achieve the desired particle size. Additionally, a rotary grinder was used for shredding plastics to fine aggregates of less than 500 µm [39]. Chen et al., proposed a simple method of processing waste plastic in concrete mixes. The waste plastics were directly placed in a screw extruder and pelletized without any mechanical size reduction. Together with the filler and coupling agents, the pellets were again passed through the extruder machine. The initial size of the plastics was not important as the plastics melted and different segments stuck together to form homogeneous pellets [40]. It is noteworthy that mechanical size reduction, shredding or pelletization makes it easier for the fine plastic particles to mix with solid material before heating. When the plastic composition, on melting, becomes viscous, it becomes a challenge to mix with other aggregates such as concrete, stone and sand [35]. Thus, the mix design is important to ensure plastics mix homogeneously throughout the composite to give a good matrix and effectively improve the mechanical strength.

Chemical compounds such as sodium hydroxide and sodium hypochlorite have been used to treat the surfaces of plastics prior to mixing with construction mixtures [41]. Plastics are expected to mix physically with concrete mixtures rather than form chemical bonds. However, oxidising agents such as sodium hydroxide enables a chemical reaction to occur between the polymer chains and the concrete by modifying the polymer surface functional groups. The polymers can also contain ionic groups (hydroxide, oxide) that will bind to the concrete [41]. Choi et al., treated shredded PET bottles between 5-15 mm with ground granulated blast furnace slag (GGBS). The aim was to solidify the aggregate with GGBS and foster a reaction which resulted in formation of a pozzolanic material due to the strengthening of the interfacial zone between a cement paste and the aggregate [42].

2.1.1.2 Properties of construction composites with waste plastics

The plastic wastes are incorporated as aggregates, binders, or molds in construction materials (Table 2.2). As aggregates, plastic wastes were found to be favorable in reducing the cost of concrete, improving resistance to impact loading and changing the modes of failure of concrete from brittle to ductile [8]. Furthermore, waste plastics can be incorporated in bricks

to improve their porosity while firing and to reinforce bricks under ambient temperatures [24]. PET waste plastic was reported to improve resistance to corrosion especially against sulfuric acid and also found to make the concrete lighter [43]. In plastic-related studies waste materials were prepared by cutting or shredding them into narrow strips or little fibers in a range of a few millimeters [24]. Limami et al., used HDPE and PET as fine aggregates (1-6 mm) in unburnt clay bricks [44]. Xu et al., used expandable polystyrene (PS) (3 mm) to manufacture lightweight concrete and bricks [45].

In brick and concrete production, waste plastics partially replace one or more of the conventional materials. The replacement ratios are typically from 0.1 to 15%, although in some studies up to 80% waste plastic has been used as a binder material [46]. For example, Hannawi et al., replaced sand with 3%, 10%, 20% and 50% of PC and PET waste plastic in mortar [47]. Natural aggregates were partially replaced with PET in burnt clay bricks [48]. It was observed that concentrations above 15% of PET led to disintegration of the bricks at high temperature. Thus, concentrations less than 15% PET were optimum for fired clay bricks using controlled conditions [48].

Table 2.2: Physical properties of recycled plastics and their possible construction applications [34]

Plastic	Physical properties	Possible construction application
High-density polyethylene (HDPE)	Rigid	Plastic lumber, table, chairs
Low-density polyethylene (LDPE)	Flexible	Bricks, blocks, stepping stones, pillars
Polypropylene (PP)	Hard and flexible	Aggregate in asphalt mixtures
Polystyrene (PS)	Hard and brittle	Insulation material
Polyethylene terephthalate (PET)	Hard and flexible	Fibres in cementitious materials
Polycarbonate (PC)	Hard and rigid	Aggregates in cementitious materials

The incorporation of plastic waste into construction composites has environmental benefits of reducing pollution and producing new construction materials with distinct properties compared to conventional materials. Belmokaddem et al., studied the mechanical and physical properties of concrete containing plastic waste aggregates. Three types of plastic waste were used (i.e. HDPE, PET and polyvinyl chloride (PVC)) to substitute natural aggregates

in different amounts (25, 50 and 75%) [49]. It was noted that the use of plastic waste reduced the density of the composite and the lowest dynamic elastic modulus was recorded for composites containing 75% HDPE, which corresponds to a more ductile composite. The lowered dynamic elastic modulus resulted in more deformable concrete composites which can be used in flexible structures. An improved thermal insulation was detected using composites with 75% PVC and all the composites containing plastic aggregates showed a low heat capacity. This suggests the use of these materials as durable concrete pavements that alleviate the night-time island effects due to high temperature differences between daytime and nighttime. However, a decline in the compressive strength upon an increase in plastic aggregate substitution was noted [49]. It is noteworthy that the concrete and bricks with waste plastics still showed a relatively high compressive strength which is acceptable according to building and construction standards. Mondal et al., observed a decline in the compressive strength of bricks from 34 MPa to 17 MPa upon addition of 0-10 wt. % polycarbonates, polystyrenes and mixed plastics [50]. Interestingly, Herki et al., detected no change in the concrete compressive strength up to 30 wt. % waste using expanded polystyrene replacement [51]. In another study, 3 wt. % polypropylene waste plastic was found to be the maximum for sand replacement in burnt clay bricks [52].

Plastic replacement optimization studies are required to ensure that the properties of the construction composite meet those of the desired application. Table 2.3 shows the application of waste plastic in bricks using various replacement ratios. In sand bricks, waste plastics are used as binders without the use of cement or pozzolanic aggregates.

Bricks are classified according to their properties, which informs their application. First-class bricks refer to bricks with a compressive strength of about 14 MPa, with a water absorption rate of not more than 20% when immersed in water for 24 h. These bricks are great for flooring and external walls applications [52]. Bricks with compressive strength of not less than 7 MPa and water absorption of not more than 22% are classified as second class. This type is not necessarily preferred for flooring, but good for walls that do not require plastering. The third class of bricks has a compressive strength that ranges between 3.5-7 MPa, with water absorption of not more than 26% and are used in ordinary construction. Class four bricks have low porosity and strength of about 15 MPa, this type is not good for building purposes and usually applied in road construction [52].

Alaloul et al., investigated the effect of polyethylene terephthalate (PET) and polyurethane (PU) on the mechanical strength and thermal stability of interlocking bricks. A compressive strength of 5.3 MPa was obtained for a PET/PU brick with a 60:40 ratio, suitable for a non-load bearing masonry brick wall such as a partition wall. A low thermal conductivity of 0.153 W/mK was achieved for a PET/PU brick with a 80:20 ratio which signifies a good thermal insulating material [53]. Bharathi et al., obtained a compressive strength of 55.91 MPa which is 88.59% higher than the standard clay bricks, upon employment of 60 wt. % waste plastic in sand bricks. The water absorption was also reduced from 19.8% of conventional bricks to 0.452%. The properties of waste plastics thus show their potential application in different types of innovative building and pavement bricks.

Table 2.3: Recent applications of waste plastic in bricks

Polymer	Replacement %	Type of replacement	Other materials	Application	Brick dimensions (mm)	Test performed	Ref
PP	1-5	Shreds	Crushed glass, clay	Aggregate	150 × 100 × 63	Water Absorption, Shrinkage, Mechanical strength	[52]
PET& PU	60:40	Shreds	-	Binder	64 × 13 × 3.2	compressive strength, impact, flexural strength and thermal conductivity	[53]
LDPE	20	Pellets	Sand, cement	Aggregate	40 × 20 × 10	Compressive strength Water absorption Drag strength	[31]
PET	30, 20	Shreds	Sand	Binder	222 × 106 × 73	Durability through acid,	[54]

						Water absorption Compressive Tensile strength	
PP & PE	10-30	Shreds	Sand	Binder	200 × 195 × 100	compressive strength, efflorescence, water absorption, soundness, fire resistance test	[55]
LDPE	33.33- 66.67	Shreds	Sand	Binder	200 × 150 × 100	Thermal conductivity Bending stress	[56]
HDPE	100	Shreds	-	-	240 × 120 × 60	Compressive strength Thermal properties Fire resistance test	[57]
LDPE	5-20	Shreds	Sand, cement, coal fly ash	Aggregate	190 × 90 × 90	Compressive strength Water absorption Efflorescence test Soundness test Crushing test	[58]

*PP: polypropylene, PET: polyethylene terephthalate, PU: polyurethane, LDPE: low density polyethylene HDPE: high density polyethylene

2.1.2 Coal fly ash

Coal fly ash (FA) is a cementitious coal combustion by-product produced by thermal power plants in large volumes [59]. Fly ash dumps take up space and cause contamination of the

environment in the long term. Its disposal is not sustainable because it is costly and soon will be forbidden. Although fly ash is considered a waste product, it has been used in the production of valuable products. This is due to its cementitious, alkaline and pozzolanic properties [60]. The utilization of fly ash as an environmentally benign product has received great attention, since it is freely available, cheap, and would reduce its environmental impact (pollution and wasted land) [60]. In South Africa, fly ash is mainly used in the cement and concrete industry. Other limited applications of fly ash are in soil stabilization, agriculture, low-cost adsorbents and for the synthesis of zeolites and geopolymers [61].

2.1.2.1 Properties of coal fly ash

The appearance of fly ash varies from grey to black, and its colour gives information about its properties and composition [61]. Fly ash consists of small particles (0.5-200 μm) as a result of the combustion process, coal source etc. and is mostly alkaline and refractory in nature [60]. It is spherical in shape and contains irregularly shaped minerals and unburnt carbon. The hollow cenospheres and irregularly unburned carbon content tends to have larger sizes as shown in Figure 2.3. Moreover, fly ash with lower calcium levels is normally coarser than high-calcium ashes. The specific surface area of fly ash is 150 m^2/kg for mechanically collected fly ashes and 1200 m^2/kg for ones collected by electrostatic precipitators. Its specific gravity is in the range of 1.90 to 2.96 for subbituminous ash and iron-rich bituminous ash respectively [62].

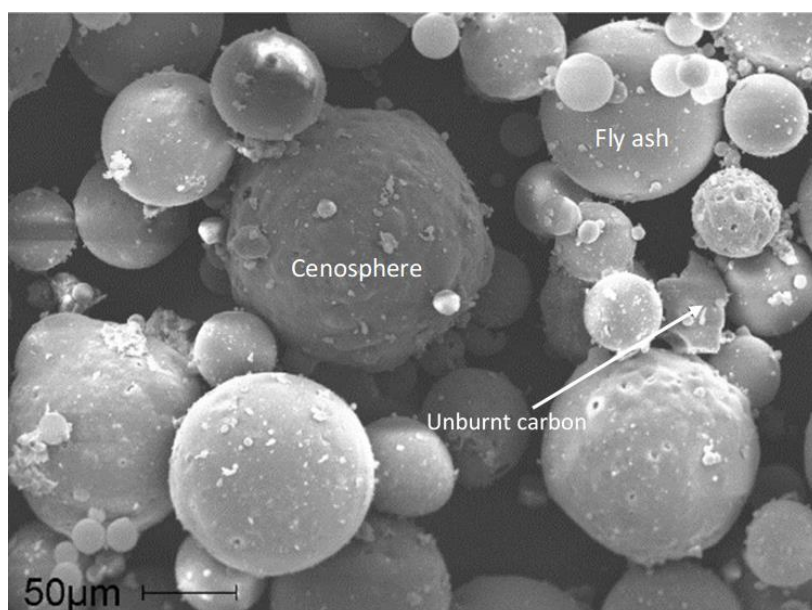


Figure 2.3: SEM image of a representative sample of coal fly ash particles in the range of 10–100 μm [63]

The main components in fly ash are silicon (Si) and aluminium (Al) with minor amounts of sulphur (S), sodium (Na), iron (Fe), titanium (Ti), phosphorus (P) and calcium (Ca) [64]. Fly ash also contains trace amounts of elements, such as chromium (Cr), barium (Ba), nickel (Ni), palladium (Pb), strontium (Sr), vanadium (V) and zinc (Zn). The major mineral compound in fly ash is amorphous aluminosilicate (glass) and the major crystalline minerals are quartz and mullite. Other crystalline minerals present in fly ash include but are not limited to, anhydrides, hematite, feldspars, periclase, wollastonite, cristobalite and lime [65]. The composition of fly ash depends on factors such as the type of coal burnt, the process of which the coal undergoes before and during the combustion process [66]. Mullite is produced during coal combustion of decomposed clays, and doesn't normally contribute in the cementing reaction because of its low reactivity. Similarly, quartz is generally unreactive during the fly ash hydration. Classification in terms of surface chemistry, mineralogy, composition, and reactivity is significant for fly ash applications [64,67]. Notably, South African fly ash is reported to have high concentration of silica (SiO_2) and alumina (Al_2O_3), making it suitable in the construction industry and as a zeolite precursor.

According to the American Society for Testing Materials (ASTM), fly ash can be classified based on its chemical composition (*i.e.*, SiO_2 , Al_2O_3 calcium oxide (CaO) and iron oxide (Fe_2O_3))

content) into two categories, namely Class C and Class F (Table 2.4). Class C fly ash is normally produced from the combustion of lignite or sub-bituminous coal. It contains between 50 and 70 wt.% of SiO_2 , Al_2O_3 and Fe_2O_3 and the fly ash also has a high lime content. Class F fly ash is formed from the combustion of harder, older anthracite and bituminous coal. It contains more than 70 wt.% of SiO_2 , Al_2O_3 and Fe_2O_3 and has a low content of lime.

Table 2.4: Classification of coal fly ash according to ASTM

Property	Fly ash class	
	Class C	Class F
Silicon dioxide (SiO_2) + aluminium oxide (Al_2O_3) + Iron oxide (Fe_2O_3), min. (%)	50	70
Sulphur trioxide (SO_3), max. (%)	5	5
Moisture Content, max. (%)	3	3
Loss on ignition, max. (%)	6	6
Available Alkalis (as NaOH) max. (%)	1.5	1.5

A cement agent like cement, hydrated lime or quicklime are required for Class F coal fly ash in order to possess cementitious properties. The incorporation of sodium silicate as an alkali activator to Class F coal fly ash may result in geopolymerization. The combustion of younger sub-bituminous coal results in high calcium fly ash with pozzolanic and self-cementing properties. Furthermore, higher contents of sulphur were also found to be beneficial in enhancing the self-cementitious strength of fly ash [68]. Class C coal fly ash has increased strength over time in the presence of water. More than 20% lime (calcium oxide) is possessed by Class C coal fly ash. Thus, unlike Class F fly ash, an activator is not required for self-cementing Class C coal fly ash because of the higher content of alkali and sulfate [69]. However, coal fly ash with low calcium content has been used in the production of geopolymers or as an admixture in concrete and has shown good performance [62]. High calcium fly ash has been suggested to contribute to premature distress in concrete. The instability in concrete caused by high levels of calcium oxide is a major concern which hinders fly ash applications [62].

2.1.2.3 Application of coal fly ash in construction composites

In the construction industry, fly ash has been applied as either a raw material or additive in cement products. It is useful in the substitution or replacement of cement in concrete and other building applications due to its pozzolanic properties [70]. The incorporation of fly ash as an aggregate enhances workability and minimizes the bleeding of freshly mixed concrete. Class F fly ash replacement of cement reduces the heat of hydration and the possibility of cracking in concrete in its early stage of formation [71]. Hardened fly ash composites have great strength and low permeability [72]. Furthermore, the addition of fly ash could save production costs.

According to the ASTM the maximum loss on ignition (LOI) of fly ash should be 6% (Table 2.4) for application in concrete. LOI gives an indication of the residual carbon in the fly ash. Furthermore, LOI values also provides an indication on the presence of carbonates and water in clay minerals. However, the main contributing factor is the carbon combustion [73]. LOI of the carbon content and the fineness of the material are two properties of concern in using fly ash. They are often interdependent because a high carbon content (high LOI) results in a coarser fly ash due to the coarse carbon particles [74]. The residual carbon and coarser particles present in the fly ash can affect its pozzolanic properties by absorbing water and chemical admixtures (e.g., superplasticizers), thus reducing their efficiency [75]. Subsequently, the strength development of concrete is negatively affected by low quality fly ash with high LOI and large particle sizes [76]. Typically, fly ash-based composites show quasi-brittle behavior as a result of their ceramic-like properties, which includes low tensile strength and fracture toughness [77].

The replacement of fly ash varies according to its intended purpose. Typically, the additive amount can range from 15-35 wt%. The replacement can go up to 70 wt% for pavements, walls and parking lots and even up to 80 wt% for autoclaved aerated concrete [78]. The higher replacement of fly ash in large structures helps avoid temperature rise of concrete. Recent applications of coal fly ash in bricks and the tests performed on the specimens are shown in Table 2.5. Like clay, fly ash is rich in Al and Si, and has a great potential to be used as a precursor for the synthesis of sustainable geopolymer bricks. Iftikhar et al., replaced 0 to 100 wt% of clay with fly ash to develop sustainable green bricks. The bricks with 30 to 60 wt% fly

ash were observed to have low density, allowable water absorption and high compressive strength and could be applied for load bearing purposes [11]. Furthermore, the resultant geopolymer bricks had enhanced physical and mechanical properties relative to traditional clay bricks [11]. The ASTM data suggests that a good brick should possess compressive strength of 3.5 MPa and its water absorption should not be more than 20% of its weight. Evarasan et al., incorporated 40 wt% of fly ash in clay bricks and observed a water absorption of 13.28% and compressive strength greater than 3.5 MPa for the synthesized bricks [79]. In another study, fly ash/lime bricks were produced in a steam autoclave. Lime was used as a binding agent and tobermorite and katoite were formed as binding phases in bricks. The optimum brick produced from 88% of ash, 12% lime and 20% water exhibited a compressive strength of 7.5 MPa [80].

Previously, various tests have been carried out and it was found that the optimal ratio to produce bricks from fly ash, bottom ash and cement is 1:1:0.45. Compressive strengths of between 7.13 and 17.36 MPa were obtained with ultra-velocity pulse ranging from 2.20 to 2.96 km/s. Fire resistance tests revealed that the bricks did not show any spalling, and, after heating the strength increased up to 30% [81]. In another study, high volumes of fly ash of above 50% were used to replace clay. The bricks showed high compressive strength, low water absorption, no cracking due to lime, no frost effects and a high resistance to frost-melting of the brick [82].

Table 2.5: Recent applications of coal fly ash in bricks

Class	Replacement %	Other materials	Brick dimensions (mm)	Test performed	Ref
F	10-50	Clay	30 × 10 × 60	Compressive strength Linear shrinkage Loss on ignition Water absorption Leaching Microstructure	[83]

F	10-30	Waste slug, cement, polypropylene fibers	80 × 40 × 80	Compressive strength Bending strength Shrinkage	[84]
	10,12,16	Cement, lime, wood	-	Compressive strength Water absorption Shrinkage Density	[85]
	10	Cement, sand, palm oil clinker	-	Compressive strength Microstructure Flexural strength Water absorption	[86]
C	2-8	Clay, glass	140 × 65 × 40	Compressive strength Porosity Shrinkage Density	[87]
F	7	Stone dust, lime	190 × 90 × 90	Compressive strength Density Water absorption Percentage voids Efflorescence Modulus of elasticity Shrinkage Impact energy	[88]
F	10-100	Black cotton, granite waste	210 × 100 × 70	Compressive strength Efflorescence Water absorption Weight analysis	[89]
F	85-95	Cigarette butts	50 × 50 × 50	Compressive strength Density Water absorption Microstructure	[90]

C	80-90	Waste brick powder	50 × 50 × 50	Compressive strength Absorption Flow Microstructure	[91]
F	80	Sand	240 x 115 x 53	Porosity Microstructure	[92]

2.1.3 Other waste materials

Apart from plastic and coal fly ash discussed above, there are many other waste materials that have been used in construction composites to reduce the amount of natural aggregates required and to beneficiate waste (Table 2.6). These waste additives used in bricks are typically classified as sewage sludge, ash, inorganic residues and organic wastes [93]. The use of waste materials with silica in clay bricks to act as fluxing agents has been of particular interest. The silica binds clay particles at relatively low temperature and reduce the energy consumption in brick manufacturing [93].

Waste glass has been employed in burnt clay bricks as an additive. Typically, waste glass is added to brick samples in the range of 0.5 to 94 wt. %. However, most studies usually focus in the range of 5 to 20 wt. %, with the glass particle size between 45-600 µm [94]. The glass incorporated bricks are typically shaped through three methods: moulding, pressing and extruding. A pressure of about 1 to 40 MPa is applied during the pressing method to produce samples. Once, the samples are shaped, they are fired and dried at 100-110 °C for between 3 hours to 3 days [94]. It was found that shrinkage increased as the percentage glass by mass increased, and as the firing temperature increased. For larger particles (greater than 132 µm) the shrinkage decreased due to incomplete sintering [94]. The incorporation of waste glass has allowed bricks with enhanced compressive strength and low water absorption to be obtained [95].

Agricultural waste such as rich husk and sugarcane bagasse have been employed in the manufacturing of bricks. Even though these waste products compromise the strength and increase the water absorption of clay bricks; they result in lighter bricks that produce more energy efficient structures due to the enhanced insulation properties [96]. Gorhan et al., [97] studied the effect of rice husks on the porosity and thermal properties of clay fired bricks. It

was observed that the bricks with 5% and 10% addition of rice husk exhibited a compressive strength of 7–10 MPa which is smaller than the reference clay bricks. However, these results still satisfy the building and construction requirements. Samples made using finer rice husks (up to 10%) had higher mechanical strength and thermal conductivity than coarser samples [97]. Similar observations of reduced compressive strength were made by Kazmi et al. [98], upon the addition of agro-waste (sugarcane bagasse ash and rice husk) to clay bricks. The waste was incorporated at 5%, 10% and 15% by clay weight. It was found that 5% addition of sugarcane bagasse ash and rice husk was the optimum addition to produce bricks that met the ASTM requirements. Furthermore, the bricks showed resistance to efflorescence and microscopic analysis showed the specimens to be porous, consistent with the formation of lighter bricks [98]. Interestingly, several waste materials incorporated in bricks produces light bricks which are preferred in earth quake areas [99].

Table 2.6: Recent applications of waste additives in bricks

Type of waste	Replacement %	Specimen dimensions (mm)	Preparation conditions	Properties tested	Ref
Industrial slug	10 & 20	190 × 90 × 50	Mechanical mixing for 5 min at 8-11 moisture content, 40 MPa applied pressure, firing at 1000 & 1100 °C, soaking time of 2 h at a heating rate of 10° C/min	Compressive strength Efflorescence Porosity Water absorption	[100]
Biomass (wheat straw, olive stone flour)	6-9	75 x 80 x 75	Dried at 105 °C, fired in an electric furnace 92 °C for 1 h	Compressive strength Density Porosity Thermal conductivity Shrinkage Plasticity Loss on ignition	[101]

Waste marble	Up to 35	-	Dried and then fired at 950 °C and 1050 °C for 2 h	Shrinkage Loss on ignition Bulk density Porosity Water absorption, Compressive strength Thermal conductivity Microstructure Phase content	[102]
Agro-waste (sugarcane bagasse, rice husks)	5-15	228 × 114 × 76	Manual mixing with 20.8-22.9 % moisture content for 3h, sun-dried for 2 day and then burnt in industrial brick kiln plant at 800 °C for 36 h, conventional air cooling for 45 days	Compressive strength Thermal conductivity Water absorption Porosity Leaching toxicity Specific gravity Microstructure	[96]
Zeolite, steel slag, expanded perlite	15, 15, 50 respectively	150 × 150 × 45	Mechanical mixing at 17-21% moisture content, dried in ambient temperature for 24 h, then oven at 110 °C for 24 h, fired in an electrical furnace at 5 °C/min until 1000 °C for 1 h	Density Weight loss Shrinkage Apparent porosity Water absorption Resistance to freezing and thawing Compressive strength Thermal conductivity Microstructure	[103]
Paper pulp		-	Samples extruded through a square die (45 x 45 mm) at 10 MPa with a length of 160 mm, Oven dried at 105 °C at a rate of 5 °C/min for 24 h,	Compressive strength Porosity Thermal conductivity	[104]

			firing 900 °C and then soaking for 5 h		
Slate tailings	5	Cylinder: 36 x 36	Molding pressure of 5 MPa, 7 days curing at room temperature and 1 day curing in oven, moisture content of 15 %	Compressive strength Microstructure Water absorption Durability	[105]
Cigarette butts	1-8	Cylinder: 25 x 50	Mechanical mixing for 25 min with a 15.5% water content, compaction pressure of 240 KPa, dried at 105 °C for 24 h, fired at 1050 °C for 3 h	Thermal properties Energy savings Porosity Micro and macro structure	[106]
Tea waste	2.5-12.5	12 x 40 x 80	Mixed for 30 min with 15% moisture content, oven drying at 40 °C and 100 °C for 24 h, firing temperatures of 950 and 1050 °C	Compressive strength Thermal properties Porosity Microstructure	[107]
Glass wool	10	20 x 20 x 80	Mechanical mixing at 500 rpm for 2 min, drying for 60 °C for 24 h, demolded and further dried at 100 °C, sintered at 950 °C	Compressive strength Thermal properties Microstructure Flexural strength Water absorption Apparent density	[108]

2.2 Hybrid construction composites with engineered nanomaterials

Engineered nanomaterials are manufactured materials having at least one dimension (length, breath or height) between 1-100 nm [109]. The nanomaterials are more attractive than their bulk counterparts due their excellent inherent properties resulting from their small nanoscale sizes or dimensions. The nanoscale sizes result in a high percentage of surface atoms (relative to bulk atoms) which gives novel properties and reactivity compared to larger size materials with the same chemical composition [110]. At a nanoscale, materials exhibit unique optical,

magnetic, electrical and mechanical properties [111]. These properties allow the nanomaterials to be applied in various fields such as electronics, coatings, adhesives and reinforcement polymers [112–115].

In recent years, nanomaterials have gained popularity as reinforcement materials in building and construction composites. This is especially the case for fly ash geopolymers or waste-infused composites that are characterized by brittleness, low tensile strength and fracture toughness [62]. These nanomaterials include nano-silica (nano-SiO₂), nano-titanium dioxide (nano-TiO₂), nano-aluminium oxide (nano-Al₂O₃), nano-zinc oxide (nano-ZnO), CNTs and graphene-based materials (graphene oxide and reduced graphene oxide) [116]. Nanomaterials improve the durability, thermal, mechanical, and electrical properties of composites. Table 2.7 shows the mechanical improvements of concrete composites enhanced with nanomaterials at loadings as low as 0.5 wt. %. Furthermore, studies have shown the hydration kinetics of cement can be significantly influenced by nanoparticles, which reduces the setting time, dormant period, and increases the early strength of the cement [117].

Table 2.7: Nanomaterials in cementitious construction composites

Nanomaterial	Diameter Nm	wt.% loading	Mechanical improvements	Ref.
nano-SiO ₂	100-250	3	Compressive strength: 14%	[125]
nano-TiO ₂		5	Tensile strength: 35.6% Flexural strength: 30.3%	[126]
nano-Al ₂ O ₃	3-8	0.5	Compressive strength: 10%	[127]
nano-metakaolin	20	6	Compressive strength: 18%	[128]
nano-TiO ₂ / nano-Al ₂ O ₃	10-20	0.5-1	Compressive strength: 42% Splitting strength: 24% Flexural strength: 28%	[129]
nano- Fe ₂ O ₃	30	2-4	Compressive strength: 167% Flexural strength: 158%	[130]
nano-CuO	15	4	Compressive strength: 237%	[131]
nano-CaCO ₃			Flexural strength: 39% Fracture toughness: 41%	[132]
nano-ZnO/nano-SiO ₂	60-100	1.5-3	Compressive strength: 6.6%	[133]

Various techniques are used to test and characterize nanocomposites in order to understand their application properties. These include scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. These techniques assist in determining the morphology of the composite and the binding interaction between the nanomaterials and aggregates [118]. Mechanical properties of the nanocomposite such as tensile strength, compressive strength, bond strength and bend strength are usually tested using universal testing machine procedures [119]. Furthermore, efflorescence (salt content), flame retardancy, moisture content and density tests provide important strength data on construction composites especially bricks. The test results obtained must comply with a country's materials test standards or international standards (i.e. ASTM) for applicability in building and construction use [120].

A comparison of fillers with different particle sizes and surface areas used in concrete composites is illustrated by Figure 2.4. For the longest time, cement was deemed the finest component to bind aggregates to form composites. However, the need for better performing composites introduced the need for supplemental pozzolanic materials such as fly ash, silica fumes and metakaolin to the cement. Fibers such as carbon, glass and steel are also used in construction composites as reinforcement materials [121]. They increase the ability of composites to resist cracks by postponing the beginning of microcracks, although they are unable to stop their initiation. This is because the spacing between the fibres is large and microcracks are still able to grow [122]. However, carbon nanomaterials such as graphene and CNTs are extensively studied as reinforcements in concrete and cement composites [118,123,124]. The small particle sizes of the materials reinforce the cement matrix as their sizes are close to that of the calcium silicate hydrate (C–S–H) gel and this leads to less cracking at the nanoscale.

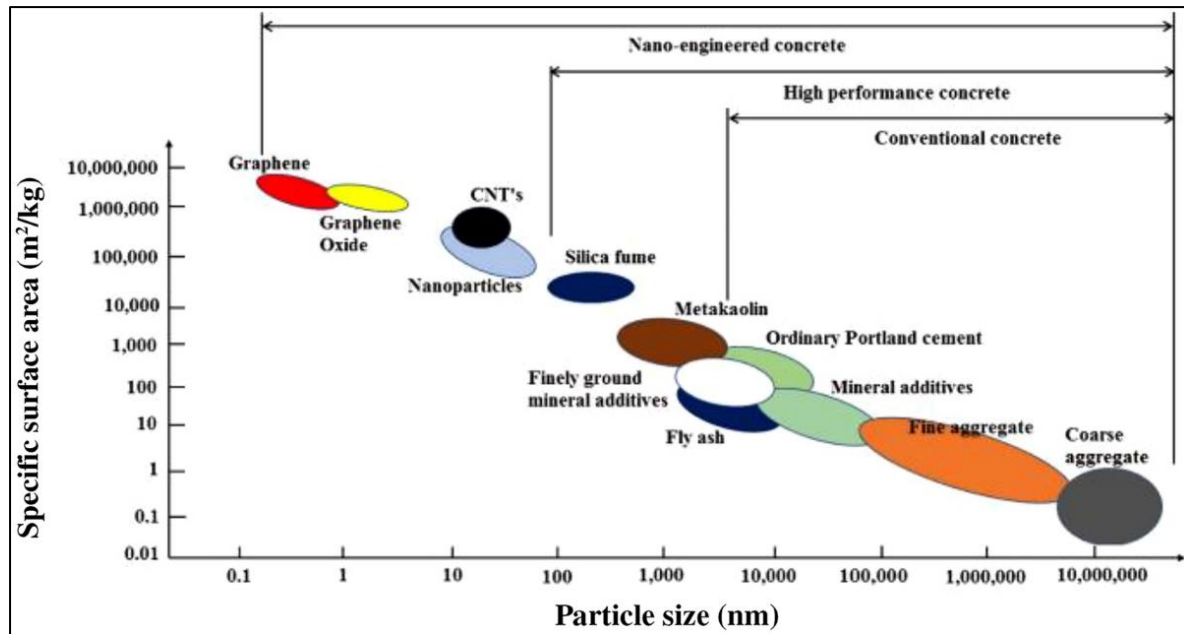


Figure 2.4: Particle size and surface area comparison of nanofillers and other aggregates in concrete [123]

Zhang et al., studied the influence of 25 nm nano-TiO₂ on the hydration and shrinkage of cement-based materials [134]. It was observed that 5 wt. % TiO₂ increased the compressive strength of cement mortar through the acceleration of cement hydration and a pore-filler effect. However, a 5 wt. % loading of the nanomaterials decreased the cement workability, resulting in the requirement of high volumes of water being required [134]. In another study, nano-TiO₂ and nano-ZnO particles (up to 1 wt. % loading) were shown to have a more limited effect on mortar fluidity as compared to nano-SiO₂ and nano-Al₂O₃. This was due to their relative lower surface areas. To overcome this, water reducing agents such as superplasticizers were used [135]. Farzadnia et al., added nano-SiO₂ to cement mortar and observed an increase in the strength development rate by 15% over 7 to 28 days of curing. The nano-SiO₂ affected the shrinkage by modifying the microstructure, increasing the hydration volume and lowering the free water content in the cement matrix [136]. Furthermore, nano-SiO₂ provided a filler effect for the calcium silicate hydrate (C-S-H) particles in the cement and acted as a strong binding agent, thus improving the interaction between the cement and the aggregate [136]. Similarly, nanoparticles enhance the fresh and hardened behavior of fly ash binders. Sequentially improving the mechanical strength of the composite [117]. The presence of graphene nanoplatelets (GNP) in a fly ash geopolymer

composite improved its resistance towards cracking (Figure 2.5). When a crack was indented on the composite surface, micro-cracks were formed. The cracks grew until they met the GNP which bridged the crack and resisted crack widening. This arose since high energy was required to open the crack, resulting in material toughening. A branching and deflection mechanism was observed, which instead of widening the crack, increased its effective length to absorb more energy and release stress [137]. This phenomenon was as a result of the high Young's modulus (2 TPa) of graphene which allowed its composite to resist the applied load and deflect the crack [137]. Furthermore, GNPs formed a bridging effect which enabled load distribution across the composite (Figure 2.5).

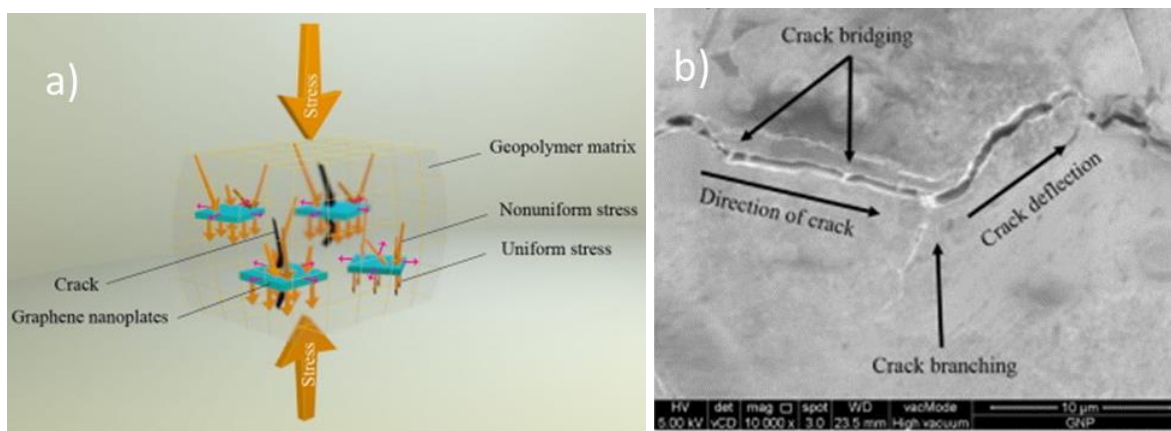


Figure 2.5: a) Schematic diagram of graphene/fly ash geopolymer composite under compression load and toughening mechanism and b) SEM image of graphene composite under stress [137]

Bricks remain an important construction material due to their versatility, durability and mechanical stability. Nanomaterials incorporated into bricks or their surfaces modified, enhances the properties of the brick. Cheraghcheshm et al., coated brick surfaces with ZnO nanoparticles and modified them with silver nanoparticles to create a hydrophobic surface as well as generate photocatalytic and anti-bacterial properties. The coated bricks showed an improvement of almost 1.8 times in flexural strength, reduced efflorescence and improved photocatalytic and antibacterial properties [138]. In another study, self-heating graphene oxide (GO) nanocomposite bricks were developed to reduce the energy associated with indoor heating which consumes energy [139]. The bricks showed superior electrical properties and improved mechanical strength from 3.15 MPa to 7.21 MPa when the GO concentration was 0.1 wt. %. An increase in graphene loading led to an increase in the heating

rate of the composite at a constant applied voltage. For example, at 1 wt. % graphene loading, the temperature increased from 22-30°C within 500 s and reached saturation. While at 5 wt. % loading, the sample heated to a higher temperature of 150°C at a shorter time (300 s) [139].

Various nanoparticles have been applied in construction composites. In this review the focus will be on CNTs, which are known to possess inherent properties that makes them suitable as reinforcing composite fillers for waste materials. Unlike, nano-SiO₂ and nano-TiO₂ which has been used in composites, CNTs have a higher aspect ratio which makes them suitable for hindering nano-size cracks.

2.2.1 Carbon Nanotubes

CNTs are 1-dimensional (1D) cylindrical carbon allotropes characterized by excellent mechanical strength, thermal stability, high aspect ratio and a high surface area [140,141]. The filler-effect due to their nanosize makes CNTs exceptional reinforcement materials in polymers and concrete composites. CNTs are lightweight materials with a tensile strength of 150 GPa, (100 times stronger than steel), which significantly improves the mechanical properties of composites [142].

CNTs exist as either single walled (SWCNTs), double walled (DWCNTs) or multiwalled (MWCNTs) according to the synthesis procedure which informs the number of rolled-up graphene sheets that make the nanotube (Figure 2.6) [143]. MWCNTs are more extensively used due to their relatively low cost, high production yield and facile synthesis procedure. They are commonly used in large application industries as they can be synthesized in large amounts [144]. For building and construction applications, industrial grade MWCNTs (low purity) compared to research grade MWCNTs (high purity) can be used. This makes the application of MWCNTs economically viable especially if the aim is towards creating affordable building materials using cheaper raw materials such as waste. SWCNTs and DWCNTs can also be applied in construction composites to improve their properties [145] but their higher production costs makes them less preferred compared to their MWCNTs counterparts.

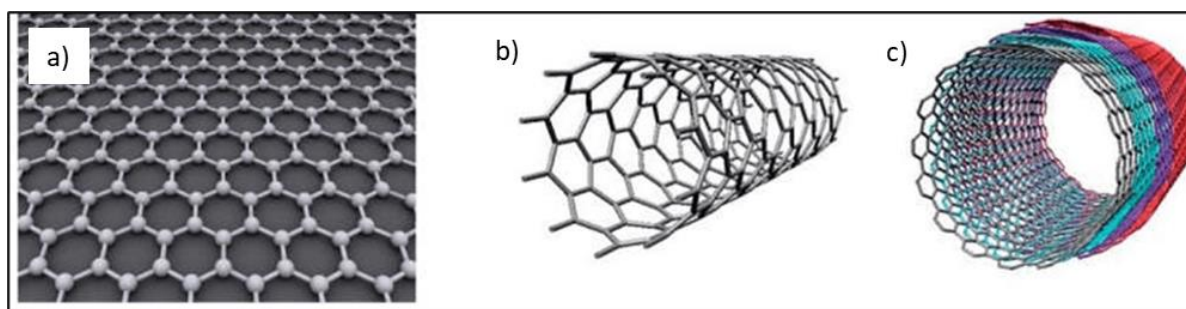


Figure 2.6: Schematic diagram of a) graphene sheet b) SWCNTs and c) MWCNTs [143]

The surfaces of CNTs have been modified and treated (functionalized) using various procedures in order to enhance their properties for application. Functionalization of CNTs result in the introduction of functional groups, alteration of electrical properties, increase in adhesion/ dispersion in composite matrix and an increase in hydrophilicity [141]. The functional groups also enhance various physicochemical properties such as chemical reactivity and solubility. Chemical functionalization of CNTs which involves covalent bonding is normally performed using strong acids (nitric or sulfuric acid) which introduces oxygenated functional groups or heteroatoms such nitrogen (N), fluorine (F) or boron (B), phosphorus (P) and sulfur as dopants [146]. Heteroatom-doping is a process in which heteroatoms replace carbon atoms within the graphitic structure of CNTs [147]. The CNTs functionalized by the covalent methods are soluble in various organic solvents because they possess polar or non-polar functional groups. Non-covalent functionalization is used to modify the interfacial properties of CNTs. The CNTs are functionalized by surfactants, polymers and aromatic compounds. This is done by employing π - π stacking or hydrophobic interactions. Non-covalent functionalization ensures that the inherent properties of CNTs are not altered, while improving their solubility significantly [148].

CNTs have been shown to be effective fillers in composites [149]. However, they do have some limitations. CNTs have large specific surface area, bending fiber-like shape, and strong van der Waals interactions, and this makes them agglomerate and entangle. CNTs are hydrophobic and thus, difficult to mix with water, organic solvents, or polymers [149]. Furthermore, the long length of CNTs and high polarizability are considered to be the deciding factor that raises the energy required to disperse CNTs within a matrix [150]. The dispersion of CNTs in a composite matrix remains a challenge and this can compromise the strength of

the composite especially at high CNT loadings [151]. This is due to difficulties of stress transfer from the matrix to the reinforced materials. Parameters that affect the quality of CNT dispersion are length, purity, entanglement, viscosity, surface modification such as functionalization, and graphitization [152]. Poor dispersibility of CNTs in a matrix can even lead to reduced mechanical strength and ultimately reduce the original properties of the composite [152]. Therefore, the reinforcement of composites by CNTs is dependent on a homogeneous dispersion in the matrix. Advances have been made in the dispersion of various nanomaterials in a polymer matrix for enhanced nanocomposite properties. However, much work is still required in the production of building and construction materials. The challenge lies in the difficulty of modifying the intermolecular interaction between nanomaterials and construction materials such as cement, clay and even fly ash, which have complex mineral and chemical structures [153]. The conventional admixtures used in the cement industry have been reported to act as dispersants and ensure that the nanomaterials are not agglomerated [121,154].

2.2.2 Dispersion methods of CNTs in composite matrix

The dispersion of CNTs in a matrix is crucial for obtaining the desired optimum mechanical strength of the composite. There are two main approaches taken to improve CNT dispersibility, namely, mechanical mixing and functionalizing of CNTs to promote interaction between the interfaces of CNTs and composite matrix [155]. Ultrasonication and acid treatment of CNTs are the most commonly used dispersion methods.

Ultrasonication of CNTs in the presence of surfactants has been used to obtain better dispersion effects. This is because, ultrasonication aids temporary dispersion of CNTs which result in re-agglomeration [156,157]. Thus, surfactants are used concurrently with ultrasonication as stabilizers to ensure CNTs remain dispersed in solution. Surfactants work by reducing the surface energy of CNTs in a solvent. Sodium dodecylbenzene sulfonates (SDBS) are commonly used as surfactants [158]. Figure 2.7 shows the dispersion of CNTs at various standing times. Poor dispersion was observed when ultrasonication was performed alone, compared to when it was performed in the presence of a sodium dodecyl sulfate (SDS)

surfactant. The CNTs remained dispersed in solution beyond 48 hours. This was expected to improve their reinforcement performance in composite matrix [159].

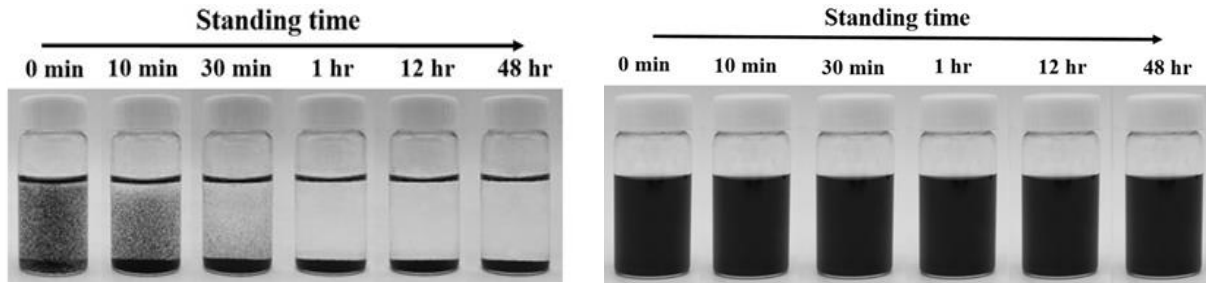


Figure 2.7: dispersion of CNTs a) ultrasonication and b) ultrasonication and SDS surfactant [159]

Ju et al., found a 1.5:1 surfactant to MWCNTs ratio to be effective for dispersion [160]. Dispersion of CNTs in surfactant solutions varied with sonication energy from 320 to 50400 J/mL, with the sonication time from 5 to 120 min [161]. In another study, CNTs were dispersed using sonication in the presence of SDBS. It was observed that the CNT dispersion was dependent on sonication energy and 2250 J/mL was found to be the optimum dispersion energy [161].

It is worth noting that ultrasonic treatment of CNTs can cause formation of a considerable number of defects in the CNTs as well as CNT buckling, bending, and formation of dislocations in the carbon structures [157]. Arrigo et al., investigated the effect of ultrasonic treatment on the structural characteristics of CNTs. It was shown that the length of CNTs was reduced with increased sonication time. The reduced CNT length affected the rheological behaviour of the nanocomposite, which progressively changed from solid-like to liquid-like upon increased sonication time [157].

In cement composites it was noted that ultrasonication and the use of superplasticizers was effective in dispersing CNTs. A study to address concerns relating to the synergistic effects between the surfactants and cement was undertaken. In the study, superplasticizers such as polyacrylic acid were used in cement composites [162]. The authors reported that the surfactant acted as both a dispersing agent for the CNTs and a plasticizing agent for the cement paste [162].

Chemical surface modification was performed on CNTs by attaching functional groups onto their surfaces to improve hydrophilicity, thus, reducing their tendency to agglomerate for improved dispersion [141]. Chemical treatment on CNTs led to better interfacial bonding between the CNT and the matrix and also enhanced the load transfer [141]. Kanagaraj et al., treated CNTs with concentrated nitric and sulfuric acid at a 1:3 ratio respectively at reflux for 30 min. The treated CNTs were further sonicated for 1 h to give better dispersion in the composite matrix [163]. Li et al., also modified MWCNTs using a nitric and sulfuric acid solution. The acid modification introduced carboxylic acid groups which induced a series of chemical reactions along the interface that enhanced the reinforcement efficiency. It was observed that using surface-treated CNTs improved the dispersion and mechanical properties (flexural and compressive strength) of the composite [119]. However, the shortfall of chemical treatment was the creation of defects on the nanotube surfaces which can compromise the CNTs intrinsic strength. Thus, less aggressive chemical treatment should be considered for application of CNTs in reinforcement composites.

2.2.3 Application of CNT- composites in construction materials

CNTs have been used in construction composites for the production of high strength composites with materials such as cement. The reinforced composite matrix has a high aspect ratio and their large surface area increases reactivity at a nanoscopic level [123]. The distribution of the CNTs in the composite is at a finer scale compared to conventional fillers. Thus, extremely low contents of CNTs can make a significant difference in tailoring the properties of composites. Low additions of MWCNTs, ranging from 0.03 to 0.5 wt. %, can present a significant improvement in the mechanical properties of construction composites. This is shown by Table 2.8, where 0.03 wt. % of MWCNTs improved flexural strength and module of elasticity by 25.1 % and 13 % respectively. It is anticipated that CNTs, when added to concrete, will increase the compressive strength beyond 200 MPa, thus enabling the construction of mile-high skyscrapers [164].

Table 2.8: Carbon nanomaterials applied in cementitious composites

Carbon nanomaterial	Dimensions (T: thickness/D: diameter/L: length)	Loading wt. %	Mechanical improvements	Ref.
Carbon nanofibers	D60- 150 nm/L30–100 μ m	0.2	flexural strength: 14% module elasticity: 23%	[165]
MWCNTs (short)	D20-40 nm/L10-30 mm	0.08	flexural strength: 25% module of elasticity: 62.5%	[122]
MWCNTs (long)	D9.5 nm /L1.5 μ m	0.03	flexural strength: 25.1% module of elasticity: 13%	[166]
		0.075	flexural strength: 49.89% module of elasticity: 31.4%	
SWCNTs		0.04	flexural strength: 4% compressive strength: 0.89%	[167]
Graphene sheets		0.025	compressive strength: 10% flexural strength: 16%	[168]
Graphene oxide	T0.8 nm/D80-260 nm	0.05	compressive strength: 47.9% flexural strength: 35.8% module elasticity: 30.2%	[169]
Graphene nanoplatelets	T1.4 nm	0.16	compressive strength: 39% flexural strength: 38%	[170]
Reduced graphene oxide (rGO)		0.05	compressive strength: 29% flexural strength: 49%	[171]

Amin et al., incorporated CNTs dispersed in surfactant (viscocrete) in cement composites at 0.02, 0.05, 0.1 and 0.2% dosages. It was observed that 0.1 % was the optimum CNT dosage and this improved the mechanical strength from 80 MPa to 110 MPa [172]. Morsy, studied the hybrid effect of CNTs on cement mortar. The cement was partially replaced with 6 wt. % nano-metakaolin and CNTs were added at 0.005, 0.02, 0.05 and 0.1 wt. %. The CNT dispersion was assisted by nano-metakaolin which enhanced the interfacial interaction between the CNTs and the cement matrix. It was observed that the CNTs were fixed to the hydration products throughout the paste. They bridged the hydration products and resisted the formation of microcracks by creating networks to transfer the load in tension. The addition of CNTs up to 0.02 wt. % improved the mechanical strength of the composite up to 11% but with additions above this level, a reduction in the mechanical strength was observed. This was

attributed to CNT agglomeration which led to microvoids and consequential weak areas [128]. In a study performed by Makar et al., SWCNTs were used in cement composites. It was observed that the SWCNTs acted as nucleating sites, with the hydration products forming on the surface of the nanotubes instead of the cement particles. This demonstrated the reinforcing behavior achieved by the presence of the SWCNTs [145].

A denser concrete was obtained when 0.1 wt. % CNTs was added to a concrete composite with waste glass and basalt fibre. An increase in compressive strength of up to 23% was recorded for the hybrid composite after 28 days of curing compared to the reference sample [173]. Chaipanich et al., studied the effect of CNTs on 20 wt.% fly ash -cement composites. At a 1 wt.% CNT dosage, the compressive strength of the fly ash cement was improved to 51.8 MPa [174]. In a recent study, acid treated MWCNTs were added to a geopolymer of coal fly ash and granulated blast furnace slag (GBFS). The functionalized MWCNTs were homogeneously dispersed in an aqueous solution containing SDS dispersant. The geopolymer was incorporated with 0.1 wt. % functionalized MWCNTs and 30% coal fly ash and GBFS. Lower water absorption, shorter setting time and higher compressive and flexural strength of 70 MPa and 9.45 MPa respectively were reported [175].

The need to reduce the reliance on non-renewable resources such as cement, which contributes significantly to carbon emissions is rather an urgent one. The utilization of waste in construction composites is a possible solution to both problems. However, the compromise in the mechanical properties of the composite (using waste) is a problem that cannot be ignored. Nanomaterials such as CNTs compensate for the strength reduction and this could enable composites made from waste and carbon nanotubes to find application in the building and construction industry.

2.2.4 CNT-fly ash nanopolymer hybrid

The understanding of the interaction of the materials within a composite is very important as it informs its reinforcement efficiency. It has been noted that the dispersion of CNTs in a composite is the major contributing factor in reinforcement [166]. The strong Van der Waals forces that exists in CNTs makes them bundle together and agglomerate in a composite matrix [176]. This compromises the strength of the composite and introduces weak spots that easily

crack when pressure/load is applied. Chaturvedi et al., observed interfacial bonding to be the interaction mechanism between fly ash-CNT nanocomposite. It was shown that the hydroxyl functionalized CNTs were well dispersed and no cracks or voids in the composite were observed (Figure 2.8), indicating strong interfacial bonding [177].

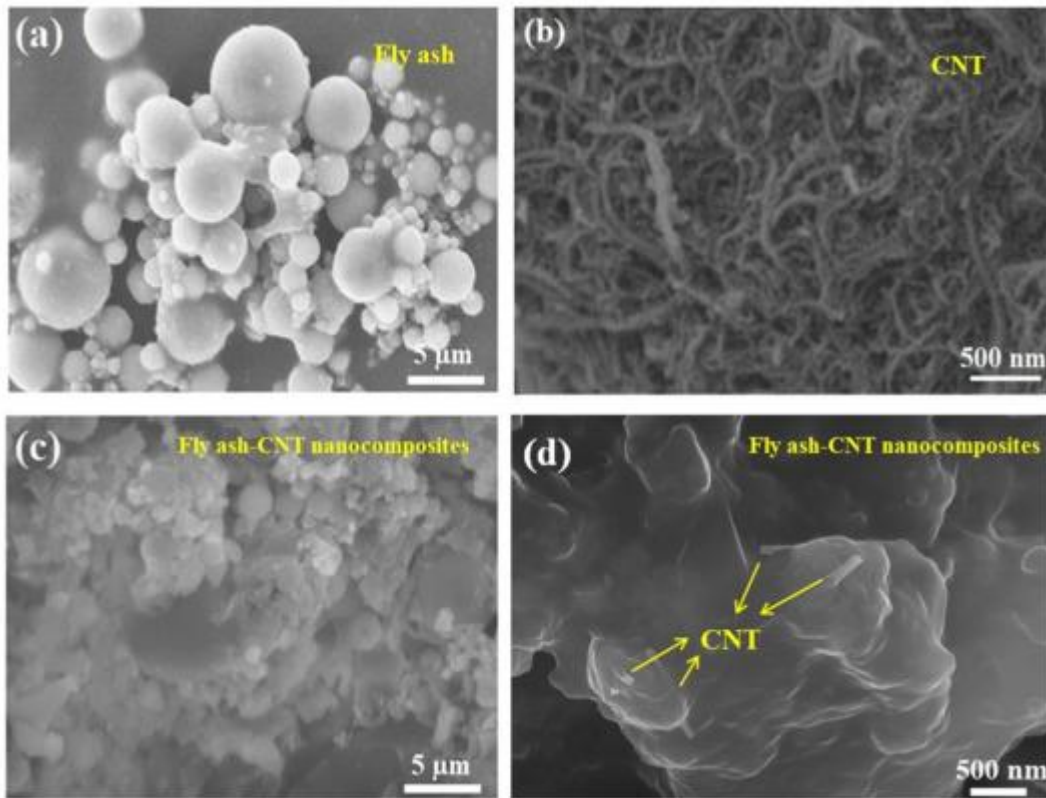


Figure 2.8: SEM images of a) fly ash, (b) CNT and (c–d) CNT-fly ash nanocomposites [177]

Salah et al., used xylene to disperse functionalized CNTs and to also dissolve HDPE. During sonication, the HDPE chains were broken and free carbon radicals might have been generated. The carboxylic ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) groups on the surface of CNTs were probably attached on the generated radicals during the sonication and dissolution processes. The attached and generated radicals further reacted with the remaining radical groups in the CNTs to form covalent and non-covalent bonding (Figure 2.9) [178]. In a hybrid composite containing coal fly ash, non-covalent (interfacial) bonding can exist within the matrix. To enhance bonding between coal fly ash and the polymer/CNT matrix, alkali activators (sodium hydroxide/sodium silicate solution) have been used [14]. This activates the SiO_2 and Al_2O_3 which are the major constituents in coal fly ash (Figure 2.9). The silica and alumina species

nucleate to form aluminosilicate oligomers which can experience interfacial adhesion to the polymer/CNT matrix to produce a hybrid nanocomposite.

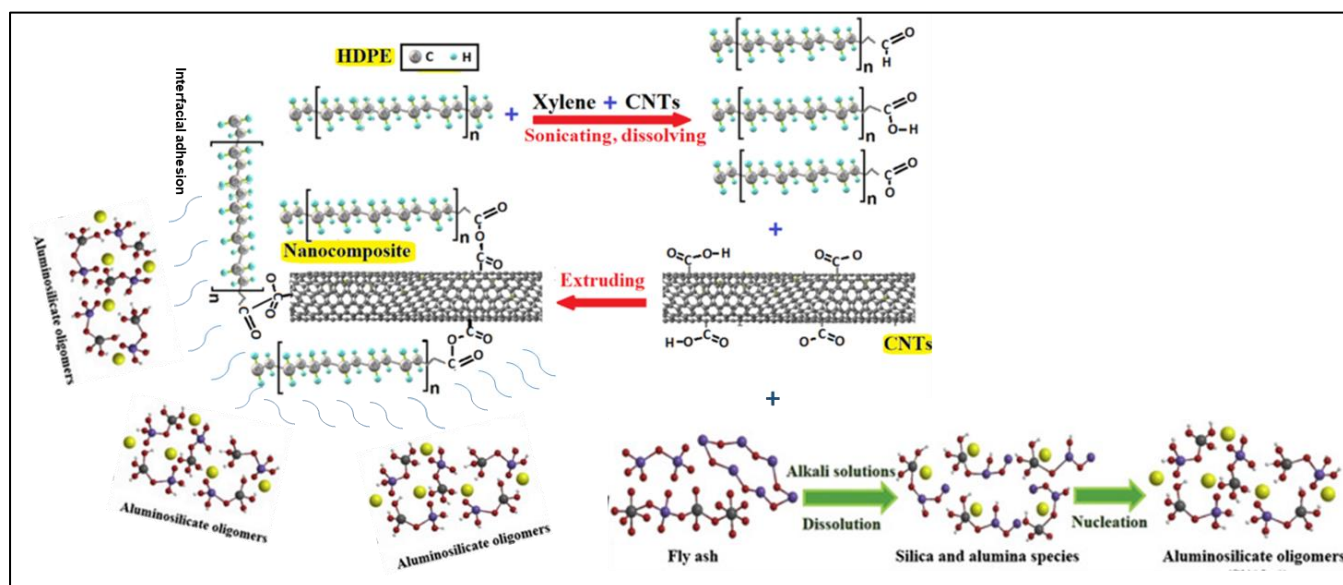


Figure 2.9: Schematic diagram of the proposed mechanism of interaction between HDPE, functionalized CNTs and alkali activated coal fly ash [14,114]

2.3 Release of CNTs to the environment

Due to their wide application, the rate at which ENMs, especially CNTs are produced, is increasing. Thus, their potential environmental release as either raw materials or from composite products must be considered. This is important because studies of their potential toxicity, which affects both the environment and human health, have gained attention [179–181]. A release assessment is critical for exposed workers, consumers and the environment. It is important for exposed individuals to protect themselves during the processing of the composites and during construction by following the set guidelines and regulations for handling nanomaterials [182]. Furthermore, to regard products as sustainable, their end-of-life must also be understood.

The release of CNTs may occur at all stages in the life cycle of the product as shown in Figure 2.10. Notably, most of the exposure and release of ENMs occurs during synthesis, while the potential release in other life cycle stages is considered to be low, but cannot be ignored

[183]. Composites are likely to undergo some form of degradation when exposed to moisture, radiation and temperature. The alteration of the matrix by degradation likely exposes CNTs to the surface of the composite and they can be potentially released to the environment [184].

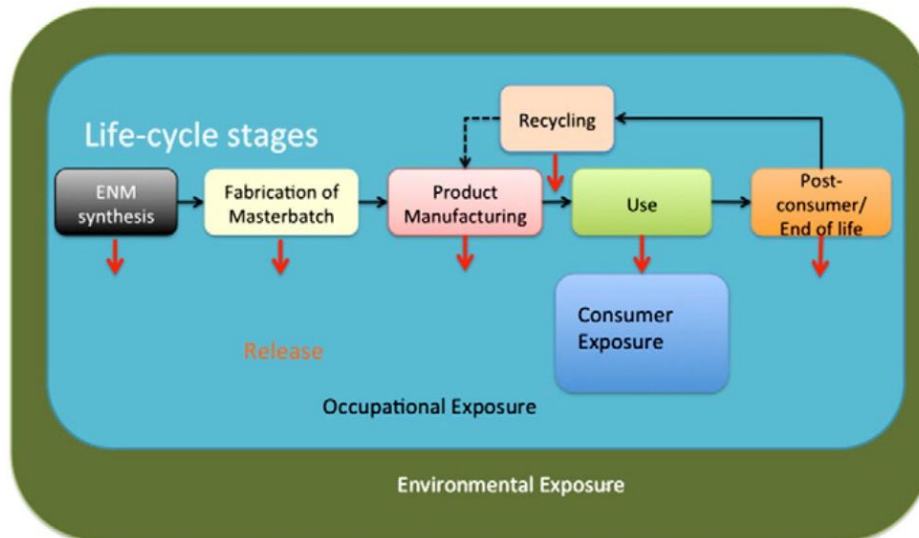


Figure 2.10: Schematic diagram of the life-cycle stages of engineered nanomaterials [183]

CNTs can be released from the nanocomposite as a result of various mechanical actions such as scratching, sanding, sawing and drilling. The Taber Abraser is used to measure the release of particles during the lifespan of the product [185]. Golanski investigated the release of carbon nanotubes from CNT/cement composites with up to a 4 wt. % dosage. Low abrasion mechanical action was simulated and no release of CNTs was detected on well dispersed samples. However, with poorly dispersed CNT samples, free standing agglomerated CNTs particles were observed under a transmission electron microscope (TEM) [186].

Weathering is another pathway to release CNTs from a composite. Weathering sources include UV-light, elevated temperatures, water absorption or a combination of these processes. This effect weakens or even degrades the nanocomposite matrix and hence exposes the CNTs to the environment [185]. Composites with CNTs and amino-functionalized CNTs were degraded with a combination of UV light and moisture [187]. The degradation of the matrix was observed by the formation of cracks shown in SEM images. The SEM images showed loose CNTs on the surface and within the cracks of the sample. The functionalized

CNTs were better dispersed than the pristine CNTs but the matrix was not very homogeneous [185]. Thus, degradation and release of the CNTs from the composite was observed.

Lastly, CNTs can be released from the composite due to inappropriate disposal by fire or by accidental combustion. This is because the CNTs have a higher decomposition temperature than most composite matrix materials. Hence, they have been used as flame retardants in building and construction composites. Likewise, CNTs have been reported to form a protective layer in composites which could offer thermal insulation [188].

Furthermore, studies on the disposal or repurposing of CNT-reinforced building and construction composites must be undertaken to ensure sustainability at the end of their life-cycle.

2.4 Summary and conclusion

The application of nanomaterials in construction composites especially construction bricks present an opportunity to transform waste materials such as plastics and fly ash into useful products. This is one sustainable way of cleaning up the environment while producing products for a wide range of applications within the built environment. The products produced from nanomaterial reinforcements such as CNTs have been reported to possess high mechanical, thermal, and water resistance properties that are desired in the industries.

More research is still required to understand the mechanism of interaction between the waste materials and nanomaterials. This will assist in understanding the physicochemical properties of the waste-nanocomposite, which will in turn affect the quality and durability of the material. Concerns such as the environmental impact of incorporating engineered nanomaterials into construction materials must be addressed if the aim is towards sustainability. Greener methods for nanomaterial synthesis must be adopted lest the aim of reducing carbon emission from cement and concrete be counterproductive. It is noteworthy that little research has been conducted on the environmental effects of CNTs in construction composites. This is a point of concern considering the rate of their application as reinforcement materials. Their potential release to the environment and any harmful effects they may pose, is not fully understood. From the above-mentioned studies, it can be noted that well-dispersed CNTs in composites are less likely to be released. Thus, efforts must be

made to ensure homogeneity of CNTs in composites to reduce their likelihood of leaching to the environment.

In summary, the benefits of nanomaterials in construction composites cannot be ignored and their utilization must be in a sustainable manner. The effects of nanomaterials in construction composites are listed below:

- Nanomaterials allow the utilization of waste even at high replacement ratio by providing reinforcement properties which compensate the loss of mechanical strength from the waste.
- Due to their large surface areas, nanomaterials are highly reactive and have been shown to accelerate hydration and provide nucleating sites that assist in reinforcing the composite. CNTs were observed to bridge the hydration products and to resist the formation of microcracks by creating networks for load transfer.
- Nanomaterials act as nanofillers and modify the microstructure of the composites which improves the overall mechanical strength.

Nanomaterials offer endless opportunities in the building and construction industry because they are engineered and can be tailored for purpose. The application of undesired waste such as coal fly ash, with high loss on ignition, can be studied with the utilization of nanomaterials. This will open more avenues for waste beneficiation and promote a more circular economy.

2.5 References

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CHAPTER 3

FACILE FLOATING CATALYST CHEMICAL VAPOUR DEPOSITION SYNTHESIS OF MULTIWALLED- CARBON NANOTUBES

3. Introduction

Carbon nanotubes can exist as single, double or multi-walled carbon nanotubes (MWCNs) depending on the number of rolled graphene sheets they were made from [1]. There are three distinct crystallographic orientations for single-walled carbon nanotubes: chiral, armchair, and zigzag [2]. Due to their diverse inherent characteristics, CNTs are used in a variety of industries, including electronics, energy storage, and reinforced composites [3]. However, the application of CNTs is still limited and mainly found in high-value products due to their high price. This is a consequence of their low productivity by most synthesis processes [4]. High-volume CNT-producing synthesis methods need to be investigated in order to expand their use on an industrial scale.

CNTs are synthesized using several techniques including arc discharge, laser ablation and chemical vapour deposition (CVD) [5]. The CVD method is the most used technique compared to the others due to its ability to generate high yields of CNTs, its affordability and good reaction controllability [6]. The CVD technique can be further categorized into catalytic chemical vapor deposition (CCVD), such as thermal (TECVD) or plasma enhanced (PECVD), oxygen assisted CVD, water-assisted CVD, microwave plasma CVD, radiofrequency CVD (RF-CVD) or hot-filament (HFCVD), high-pressure CVD (HiPco) and floating catalyst CVD (FCCVD) [7–12].

The floating catalyst chemical vapour deposition (FCCVD) method (in which the catalyst is in solution/liquid phase) offers an advantage over other synthesis methods, because it can be easily scalable to produce large volumes of CNTs that can be synthesized continuously [13]. In the FCCVD method, the catalyst and hydrocarbon precursors are added to the reactor at the same time. The catalyst e.g., ferrocene, cobaltocene or nickelocene form supersaturated vapours, that contain the metal as catalyst, after thermal decomposition. This process enables the formation of metallic nanoparticles in the vapour phase by condensation and

agglomeration of the metal atoms in the gas phase inside the reactor [14]. Since, the catalyst and carbon source are simultaneously fed into the reactor, the chances of catalyst poisoning are removed. This results in increased yields of CNTs. Furthermore, it is not necessary to have the catalyst supported on a substrate [15]. Hence, CNTs produced using the FCCVD method only have amorphous carbon/other forms of carbon and residual catalyst as an impurity and not the support/substrate, which makes it easy to purify the produced nanotubes using a simple acid treatment [16]. Lastly, since the catalyst particles are formed in a gas phase, the reaction can be performed at higher temperatures [16]. This results in the production of highly crystalline CNTs with vast potential applications. Thus, FCCVD is a favourable method to produce large volumes of highly crystalline CNTs [17].

In FCCVD, reaction parameters such as the carbon source, reaction temperature, the type of carrier gas and its flow rate and the catalyst precursor, as well as how the carbon source is introduced into the furnace can be tuned to control the structure, morphology, quality, and yield of the CNTs [18]. The catalyst can either be fed into the reactor as a supersaturated vapour, by injection, hot wire generation, spark-discharge, and mist flow [18–20]. A simple injection method has been widely adopted where the catalyst precursor and/or growth promoter are dissolved in an organic solvent that serves as a carbon source that is directly injected into the reactor at a controlled flow rate [21]. This technique is preferred due to the good homogeneity and desirable controllability of precursors that promotes the production of high quality CNTs [17].

The generally accepted growth mechanism to make CNTs using the FCCVD method starts with the high temperature decomposition of a catalyst such as ferrocene to release iron atoms [22]. The atoms experience inter-particle collisions and agglomeration to form nanoparticles of various sizes. The iron nanoparticles enhance the formation of CNTs and support the hydrocarbon's continuous pyrolysis and breakdown. The major by-product during the synthesis of CNTs is amorphous carbon which can cover the surface of the catalyst particles and deactivate them [10]. Amorphous carbon is produced as a result of an imbalance in the rate of carbon atom formation and carbon removal on the catalyst [10]. This influences the quantity and crystallinity of the as-synthesized CNTs. Optimization of reaction conditions is undertaken to reduce the amount of amorphous carbon in the final product. The other impurity in CNTs is residual metal from the catalyst. During the growth process, some of the

catalyst remains trapped within the hollow structure of the CNTs. These particles are normally removed by acid treatment with a mixture of nitric and sulfuric acid [22]. The treatment must be efficient without compromising the quality of the CNTs such as distorting their structure or shortening their length.

A simple method using only nitrogen as a carrier gas was employed in this study to produce MWCNTs. While this is a well-known process, it was required to optimize the reaction conditions with the equipment available in our own laboratory. The effect of growth temperature, injection rate and flow rate were investigated and correlated with the quality and yield of the CNTs produced. The synthesized MWCNTs were further used in a separate study as reinforcement materials in brick composites. Thus, highly crystalline CNTs which were depicted by the low I_D/I_G ratio determined from Raman spectroscopy were required for composites that would show high mechanical strength and thermal stability. Furthermore, functional groups were introduced to the surfaces of CNTs through acid treatment to improve interfacial interaction. Lastly, CNTs with long lengths were desired for the bridging effect that would reduce microcracks within the composite, to ensure their structural integrity.

3.1 Experimental

3.1.1 Materials and methodology

Afrox (South Africa) supplied the nitrogen gas (99.999%). Toluene (98%) and ferrocene (98%) were bought from Sigma Aldrich (South Africa). The materials were utilised exactly as they were supplied (neither purified nor altered).

The MWCNTs were synthesised in a horizontal floating catalyst chemical vapour deposition (FCCVD) reactor (Figure 3.1). Horizontally, the quartz tube was placed into the electrical furnace having an outlet tube attached to a gas bubble. The reaction was set at 750- 850 °C under an inert environment of N_2 adjusted between 120-150 ml/min, at atmospheric pressure. A homogeneous solution of 0.4 g ferrocene and 10 ml toluene was prepared and injected into the heated quartz tube using a syringe pump operated between 0.2-1 ml/min injection rate. In an inert atmosphere, the furnace was allowed to cool to ambient temperature once all the reaction solution was injected into the tube. After growing on the

quartz tube walls, the CNTs were gathered and weighed in a vial. The FCCVD process produced CNT bundles that resembled flaky sponges. Typically, 33% HNO₃ was used to purify the CNTs by refluxing at 90°C for 4 h. After that, the CNTs were filtered and washed until a neutral pH. Finally, the CNTs were taken for characterisation after being oven dried overnight at 110 °C.



Figure 3.1: FCCVD reaction setup a) horizontal furnace, b) syringe pump, and c) temperature control system

3.1.2 Characterization

A ZEISS Sigma 300 VP using a field emission gun scanning electron microscopy (SEM) was used to determine the morphology of the CNTs. The samples were first sputter coated with an ultra-thin layer of platinum to avoid charging. The size distribution and quality of the CNTs was studied. From the images, the shape, size, arrangement of the CNTs and the presence of other carbonaceous materials could be studied.

Transmission electron microscopy (TEM) using a Tecnai FEI T12 instrument, coupled with energy dispersive X-ray spectroscopy (EDS) capabilities was employed for the cross-sectional morphology analysis of the FCCVD synthesized CNTs. The samples were sonicated for about 10 min in ethanol and thereafter deposited on a TEM copper grid. TEM images gave information about the type of CNTs produced, the crystallinity of the product, as well as the purity data (from the EDS analysis).

Raman spectroscopy was used to provide information regarding defects, purity and crystallinity of the CNTs. A 514.5 nm argon ion laser source coupled to a charge coupled detector (CCD) was used to collect the data.

X-ray diffraction (XRD) spectroscopy using a Bruker D2 diffractometer was used to study the phase and crystallography of the synthesized CNTs. The diffraction peaks obtained from the analysis were compared with typical compounds documented in literature.

Thermal gravimetric (TGA) analysis was undertaken to study the CNT's purity and thermal stability (in air) synthesized using various conditions. A weighed mass of sample (about 10 mg) was placed into a sample holder and heated at a rate of 10 °C per minute from 0 °C to 1000 °C in the furnace chamber. A graph of temperature against weight loss (as percentage) was plotted and it gave information about the degradation temperature of the sample as well as the residual weight.

Fourier-transform infrared spectroscopy (FTIR) was employed to identify the functional groups in MWCNTs upon acid treatment modification. The FTIR spectra was recorded in the wavelength range of 500-4000 cm^{-1} using a PerkinElmer FTIR instrument. The background of the sample spectrum was corrected using a KBr spectrum.

A TriStar II Brunauer-Emmett-Teller (BET) analyser was used to measure the surface area of the CNTs. First, the samples were degassed at 150 °C for 3 h to remove any absorbed moisture. The sample's specific surface area (m^2/g) was determined through gas adsorption, where nitrogen was continuously passed over the CNTs.

3.2 Results and discussion

3.2.1 Carbon Yield

Knowledge of the yield of CNTs is crucial for their viable industrial application. It informs the efficiency of the reaction setup and whether the conditions are optimum to ensure high conversion of the hydrocarbon to CNTs as well as the efficiency of the catalyst. The equation [3.1] below was used to calculate the carbon yield of the product.

$$\% \text{ Carbon yield} = \frac{Mass_{Total} - Mass_C}{Mass_C} \times 100 \% \dots\dots\dots [3.1]$$

Where $Mass_{Total}$ = Mass of obtained sample

Mass = (volume /density)_{toluene} + (volume/density)_{ferrocene}

Mass C: Mass C in toluene + Mass C in ferrocene

In Table 3.1 and Figure 3.2, the yield of CNTs at various reaction conditions is shown. An expected trend was observed that as the temperature was increased, the yield of the CNTs also increased (Figure 1a). This was attributed to the high conversion efficiency of the toluene and ferrocene to CNTs at high temperatures. Toluene decomposes at $T > 600\text{ }^{\circ}\text{C}$, while ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) which acts as both a catalyst and carbon source starts to decompose at temperatures above $497\text{ }^{\circ}\text{C}$ [23]. It has been reported that ferrocene decomposes to methane (CH_4), cyclopentadiene (C_5H_6), hydrogen (H_2) and iron (Fe) [24]. The fragmentation begins above $497\text{ }^{\circ}\text{C}$ and different bonds break according to their binding energies. The process starts with the C-H bonds that have the lowest binding energy which release H atoms. Then follows the C-C bonds and then the Fe-C bonds. Therefore, the catalytic iron particles are only available for CNTs growth at above $500\text{ }^{\circ}\text{C}$ [25].

An opposite effect is observed (lower yield), as expected, when the injection and N_2 flow rate were increased (Figure 1b and c). This was ascribed to an insufficient residence time of the hydrocarbon in the furnace hot zone. It was also observed during the synthesis that at a high carrier gas flow rate and injection rate, the reactants were flushed to the end of the reaction tube as liquid without reacting. Thus, the resultant yield was affected.

Table 3.1: Synthesis conditions of MWCNTs

Sample	Temperature °C	Injection rate ml/min	Flow rate of N ₂ ml/min	Carbon yield %
CNTs	750	0.2	120	42
CNTs	800	0.2	120	73
CNTs	850	0.2	120	79
CNTs	850	0.5	120	49
CNTs	850	1.0	120	45
CNTs	850	0.2	140	55
CNTs	850	0.2	160	50

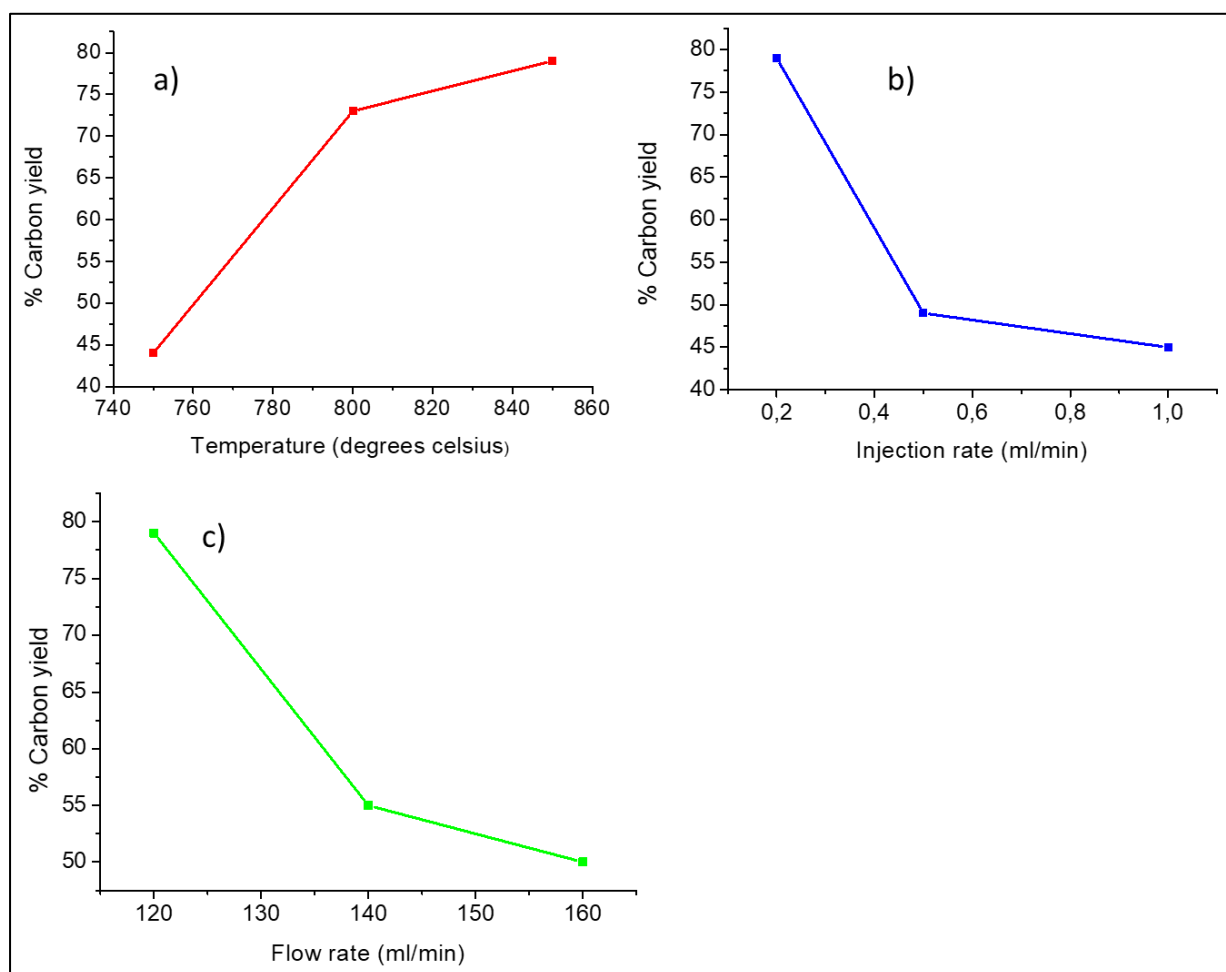


Figure 3.2: carbon yield at various a) temperature b) injection rate and c) N₂ flow rate

3.2.2 Effect of temperature

3.2.2.1 Morphology

At temperatures between 750-850 °C CNTs were synthesized to study the effect of temperature on the CNTs at constant N₂ flow rate (120 ml/min) and injection rate (0.2 ml/min). As seen in Figure 3.3, the CNTs were twisted and other carbon impurities were present at the lower temperature of 750 °C. This was because the development of highly crystalline CNTs might have been hindered by the low rate of hydrocarbon decomposition. As a result, CNTs were partially precipitated due to incomplete reaction. This is consistent with literature, where at lower temperatures of 700 and 750 °C, amorphous carbon was formed due to insufficient catalytic activity [26].

The presence of other carbonaceous/amorphous materials was reduced as the temperature was increased. Notably, sufficient energy and favourable reaction conditions allowed for the rapid cracking of the carbon source over the catalyst particles to produce crystalline CNTs [27]. As a result, more aligned CNTs of higher crystallinity were formed at 800 °C. The orientation of the catalyst particles during the first growth stage was found to be responsible for the CNT alignment [21]. CNTs synthesised at 750, 800, and 850 °C had average outer diameters of 43, 77, and 83 nm, with diameter ranges of 30–50 nm, 60–80 nm, and 80–100 nm, respectively. The size distribution was large at all the temperatures, showing that the synthesized CNTs did not have uniform diameters. An increase in temperature increased the diameter of the CNTs. There is usually an addition of carbon to the outside of the tube with an increase in temperature resulting in CNTs of larger diameters. As shown in Figure 3.3, the CNTs formed bundles due to strong van der Waal forces and had an average length of 414 micron.

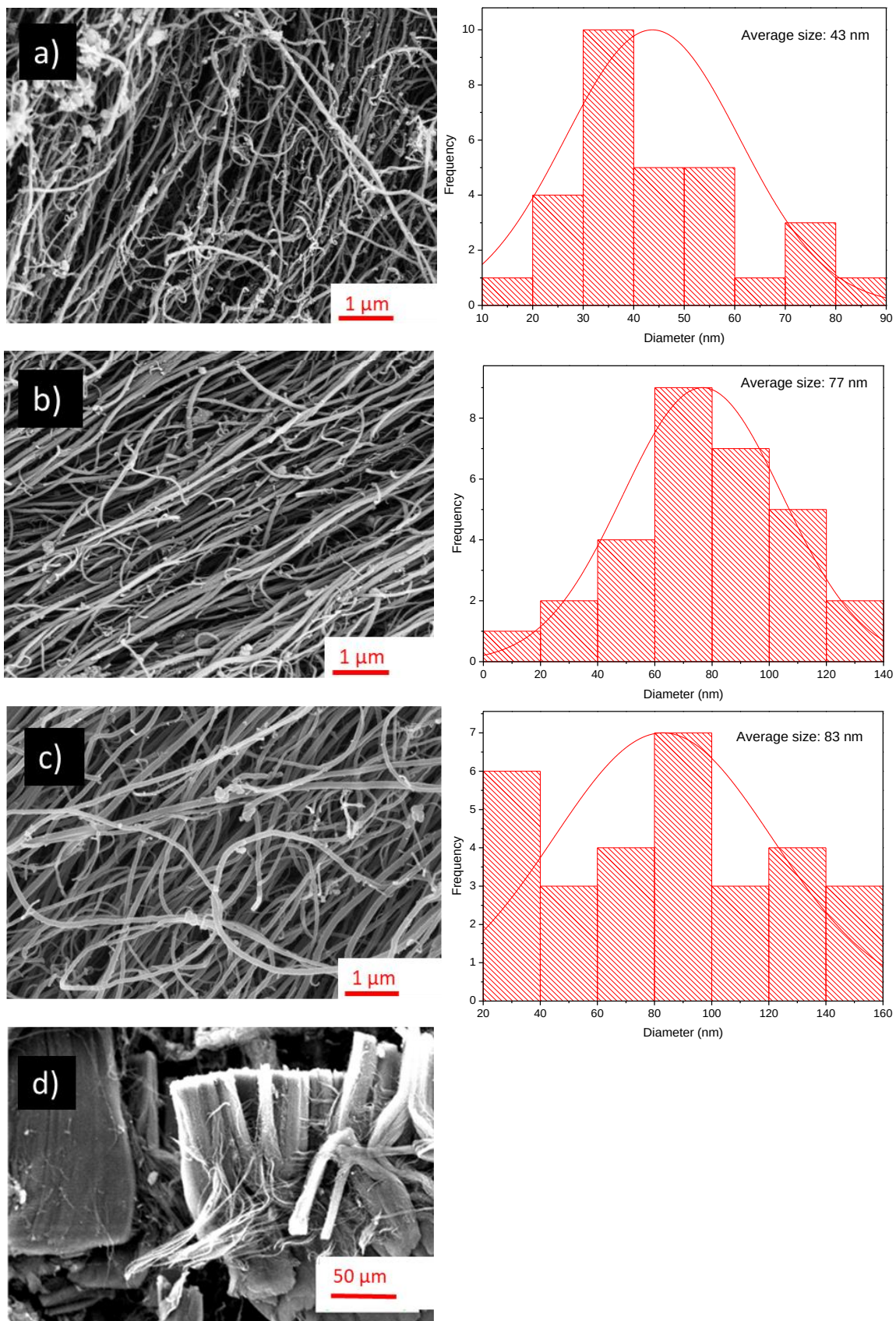


Figure 3.3: SEM images and particle size distribution histograms of CNTs synthesized at a) 750 b) 800 and c) 850 °C, while d) is a lower magnification of image CNTs synthesized at 850 °C

Figure 3.4 shows that hollow CNTs were synthesized. At 750 °C, a mixture of MWCNTs and other carbon materials was observed. It was also discovered that the hollow structure of the CNTs included residual iron particles from the catalyst. More crystalline MWCNTs formed when the temperature rose and at 850 °C, highly crystalline MWCNTs with low impurity were obtained. It was observed that the CNTs had closed-tips signifying a base-growth mechanism [28]. High resolution TEM (HRTEM) showed the multilayers of CNTs, their hollow structure and further confirmed that they had closed-tips. The average internal diameter was measured to be 22 nm. The EDS data was used to ascertain the elemental compositions of the material which informed the purity of the CNTs after acid treatment. Four elements (i.e., carbon, oxygen, iron, and copper) were detected. However, carbon was more dominant than the other elements in the sample. The copper observed was due to the grid used in the sample analysis. The expected trend was for the residual elements (Fe) to decrease with an increase in temperature [26], as more carbon was produced.

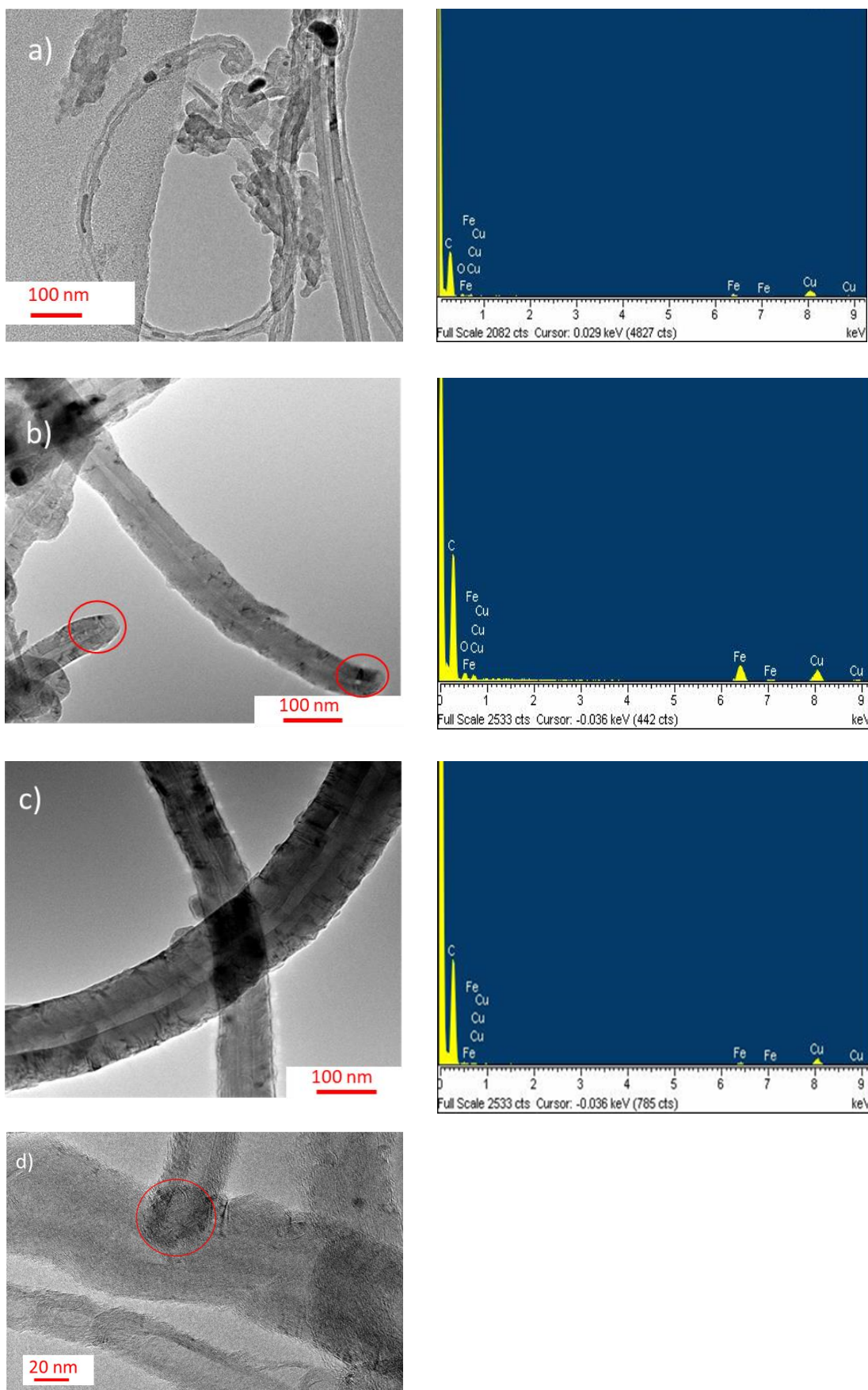


Figure 3.4: TEM images and EDS of CNTs synthesized at a) 750, b) 800 c) 850 °C and d) high-magnification HRTEM of CNTs synthesized at 850 °C.

3.2.2.2 Raman spectroscopy analysis

The Raman spectra of MWCNTs at different temperatures following synthesis are shown in Figure 3.5. There were three main bands seen: the D, G, and 2D bands. The D-band is the disorder band, which shows the proportion of symmetry-breaking defects or other impurities, particularly amorphous carbon in the case of FCCVD synthesized CNTs. The G-band, which represents the tangential vibration of carbon atoms along the CNT axis, is a feature of organised graphitic structure. The number of carbon layers in MWCNTs is often determined using the 2D-band [30]. It has been employed as one of the indirect indicators for the three-dimensional (3D) stacking of graphene layers in conventional carbon materials because it becomes asymmetric (a shoulder peak emerges) with the development of 3D stacking. The approximate locations of the D-band, G-band, and 2D band were 1355 cm^{-1} , 1577 cm^{-1} , and 2713 cm^{-1} , respectively. A direct indicator of CNT quality was the ratio of the D to G band regions [10]. It was discovered that the I_D/I_G of MWCNTs synthesised at 750, 800, and 850 °C were, respectively, 0.55, 0.49 and 0.44. I_D/I_G values for highly crystalline carbon range from 0.1 to 0.3 with a standard deviation of up to 0.2, whereas for poorly crystalline carbon, they range from 1 to 2.6 with a standard deviation of 0.8 to 1.2 [29]. The synthesized CNTs had a relatively high crystallinity, which improved with an increase in temperature. This indicated a reduction in impurities and defects as the temperature was increased.

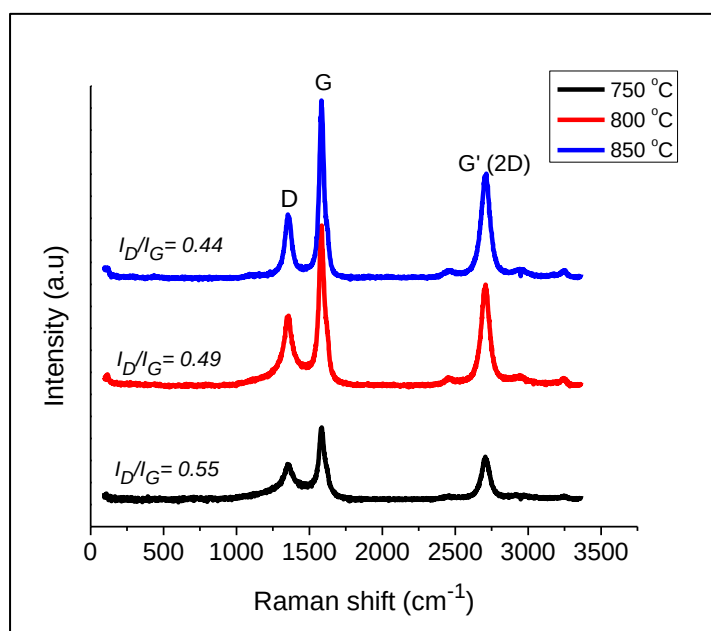


Figure 3.5: Raman spectra of CNTs synthesized at a) 750, b) 800 and c) 850 °C.

3.2.2.3 X-ray diffraction analysis

The XRD spectra of CNTs synthesised at different temperatures are shown in Figure 3.6. The graphitic peak (002) was seen at $2\theta = 26.3^\circ$, which is in line with the existence of MWCNTs because it corresponds to an inter-planner spacing of roughly 0.343 nm [30]. This pattern also shows a high degree of crystallinity, indicating a low level of impurities and amorphous carbon [31]. The (100) peak was observed at $2\theta = 47.2^\circ$ and the (004) peak was at $2\theta = 59.5^\circ$ (this was only seen for CNTs synthesized at 850 °C). the CNTs synthesized at lower temperatures, indicating an improvement in the crystalline quality of the CNTs with temperature. This indicated a progressive structural development of graphene layers at increased temperatures [30].

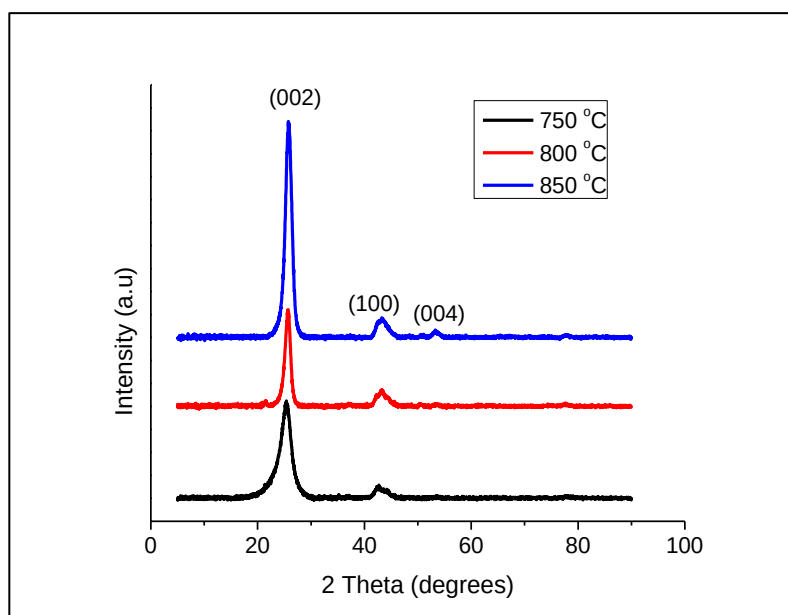


Figure 3.6: XRD spectra of CNTs synthesized at a) 750 b) 800, and c) 850 °C

3.2.2.4 Thermal analysis

It is reported that CNTs generally decompose in the temperature range of 475 and 625 °C, this depends on the reaction parameters such as the catalyst used and loadings, flow rate, reaction temperature [21]. In this study CNTs with a high oxidation temperature were produced. CNTs are more thermally stable than most other forms of carbon and defected outer layers of CNTs are oxidized at lower temperatures compared to their inner layers [32]. Thus, the temperature at which the oxidation process starts, describes the presence of

defects and impurities. Furthermore, the quality of CNTs can be defined using parameters such as diameter, length, impurities etc. The impurities in CNTs can be other forms of carbon such as amorphous carbon, graphitic particles, and metal particles from the catalyst [15].

TGA and derivative plots of MWCNTs at different synthesis temperatures are represented in Figure 3.7. As the synthesis temperature rose, so did the oxidation temperature. This implied, as evidenced by TEM and Raman data, that MWCNTs produced at higher temperatures were more crystalline. Two deterioration characteristics, at 326 and 565 °C, were noted for CNTs synthesized at 750 °C. It was suggested that the initial deterioration was caused by the decomposition of amorphous carbon, which has a low oxidation temperature [33]. The second one was ascribed to the MWCNTs' decomposition, which was responsible for the significant weight loss of 98.2%. The oxidation temperature of the CNTs made at a temperature of 750 °C was lower, signifying that the MWCNTs were more defected than those made at higher temperatures. At a synthesis temperature of 800 and 850 °C, only one degradation peak was observed (619 and 649 °C respectively) which was ascribed to the decomposition of the MWCNTs. Furthermore, it has been reported that thicker CNTs decompose at higher temperatures than thinner CNTs [34]. This is consistent with the SEM and TEM results which showed an increase in CNT diameter as the temperature was increased. The residual weight loss was 1.8%, 4.7% and 6.8% for the CNTs made at 750 °C, 850 and 800 °C, respectively. The residual weight was due to Fe₂O₃ formed from the catalyst (ferrocene) which remained entrapped in the hollow structure of CNTs as shown from the TEM images and confirmed by EDS data.

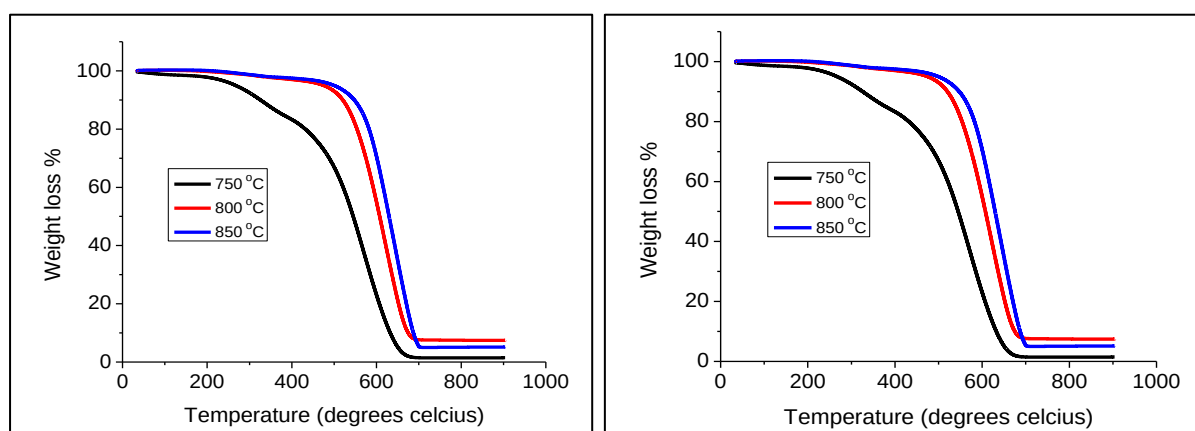


Figure 3.7: TGA and derivative plots of CNTs synthesized at various temperatures.

3.2.3 Effect of injection rate

3.2.3.1 Morphology

The injection rate of the reactants (ferrocene and toluene) was varied from 0.2-1 ml/min using a syringe pump at a constant temperature (850 °C) and N₂ flow rate (120 ml/min). The rate at which the precursors entered the heating zone of the furnace was found to affect both the quality and the quantity of the CNTs and that was investigated. Figure 3.8 shows the morphology of CNTs made at an injection rate of 0.2 ml/min. It was observed that semi-aligned CNTs were formed with minimal impurities, similar to the CNTs made at an injection rate of 0.49 ml/min. At a higher injection rate of 1 ml/min, the CNTs began to bundle up and other carbonaceous materials were also observed. This could be attributed to insufficient residence time for the hydrocarbon to decompose to produce CNTs. The injection rate also affected the yield, as the precursor was flushed out of the heating zone without sufficient reaction (as shown in Figure 3.1). The injection rate of 0.2 and 0.49 ml/min produced CNTs with comparable average diameters of 83 and 85 nm respectively. As the injection rate was further increased to 1 ml/min, the average diameter of CNTs was reduced to 60 nm.

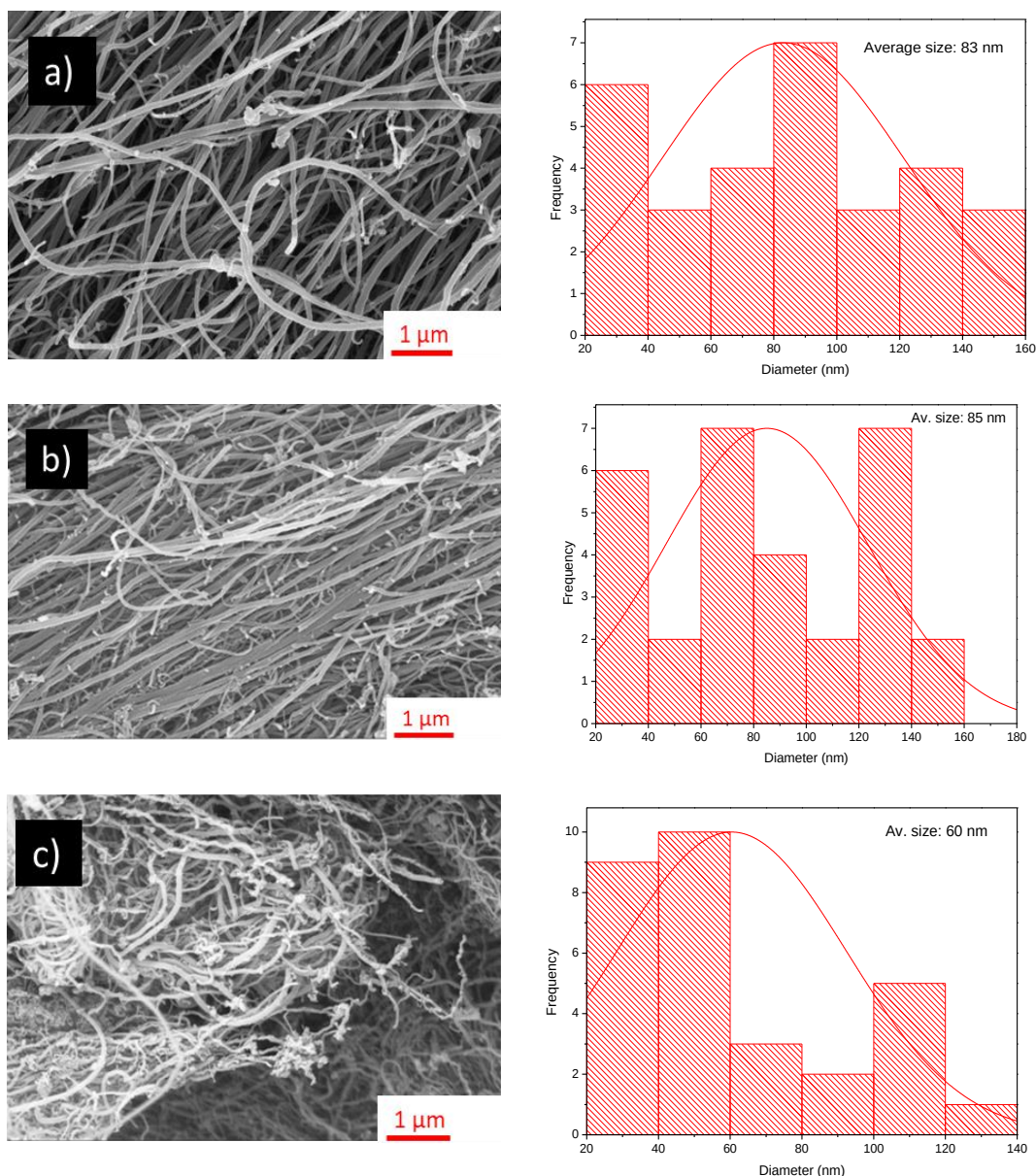


Figure 3.8: SEM images and particle size distribution histograms of CNTs synthesized at various injection rates a) 0.2 ml/min, b) 0.49 ml/min and c) 1 ml/min

The morphology and size of the CNTs changed with an increase in injection rate as shown in Figure 3.9. As the injection rate was increased, the crystallinity and purity of the CNTs was reduced. Furthermore, as also observed with SEM images, the diameter of the CNTs decreased at the higher injection rates. At 1 ml/min the structure of the CNTs became deformed and the presence of other carbonaceous/amorphous carbon was observed. The alignment of the CNTs also became distorted and the CNTs bundled-up. The EDS showed the presence of carbon, oxygen and copper and the impurity, iron. The residual iron was most abundant at a higher injection rate of 1 ml/min.

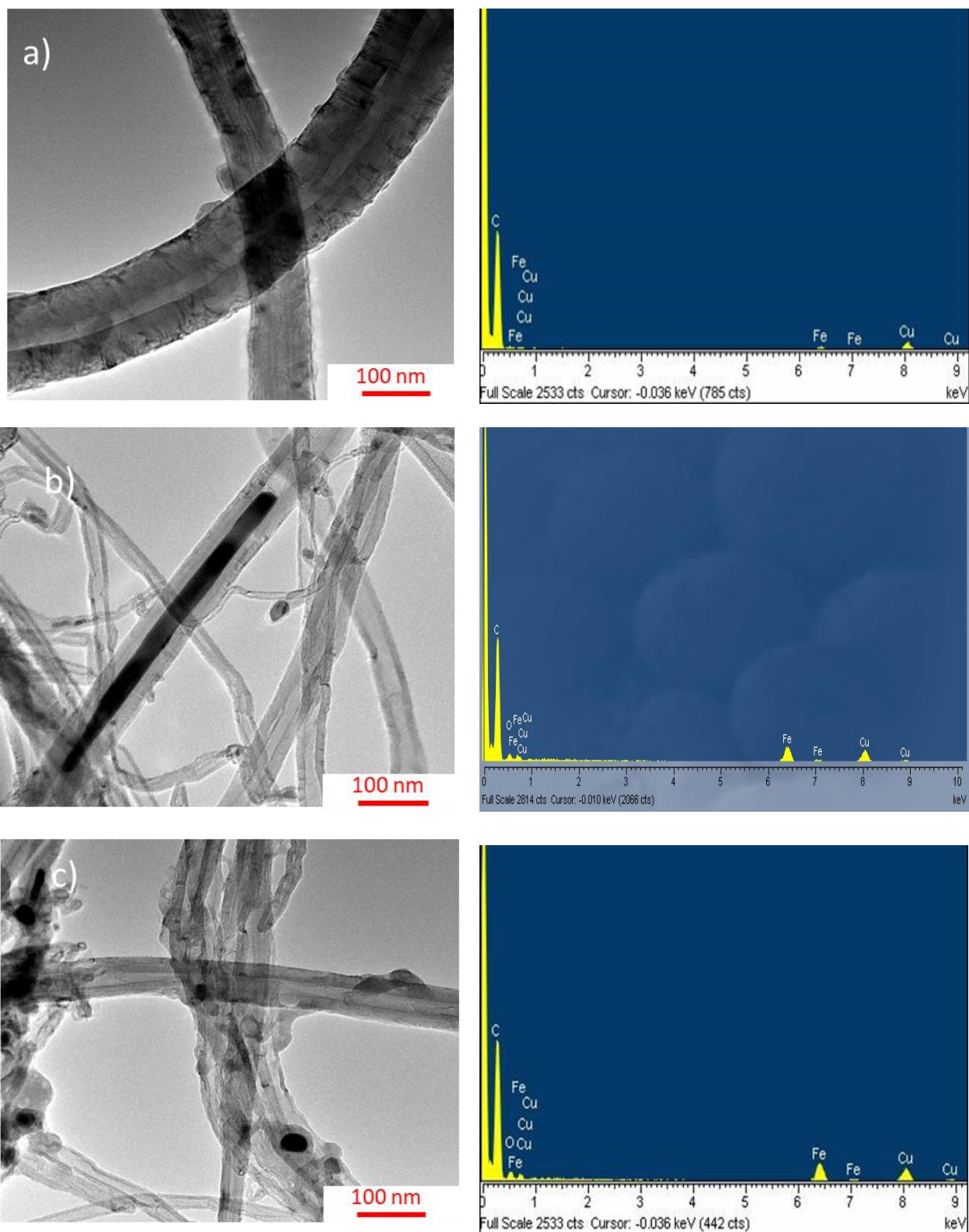


Figure 3.9: TEM images of CNTs synthesized at various injection rate a) 0.2 ml/min, b) 0.49 ml/min and c) 1 ml/min

3.2.3.2 Raman spectroscopy analysis

In Figure 3.10, the Raman spectra of MWCNTs synthesized at varied injection rates (0.2-1 ml/min) is presented. The absence of the radial breathing mode (RBM) in all the spectra was an indication that MWCNTs were synthesized, which was also confirmed by the TEM data (Figure 3.9). The RBM is a low frequency mode found in SWCNTs in regions below 300 cm^{-1} [20]. The I_D/I_G ratio was observed to increase with an increase in injection rate. This meant that the crystallinity and purity of the CNTs was reduced at increased injection rate. This was attributed to insufficient residence time for complete decomposition of carbon to produce highly crystalline CNTs. The higher CNT crystallinity at slower injection rates agreed with results obtained by Ibrahim et al., [35]. In their study, the precursor (ethanol, ferrocene and thiophene as a promoter) injection rate was varied from 3-10 ml/h. The optimum injection rate was found to be 3 ml/h and the CNTs had an I_D/I_G ratio of 0.40 [35]. Most injection rate studies are performed at ml/h. Interestingly, we have obtained comparable results at faster injection rates of ml/min, which can be attributed to easy conversion of the CNTs.

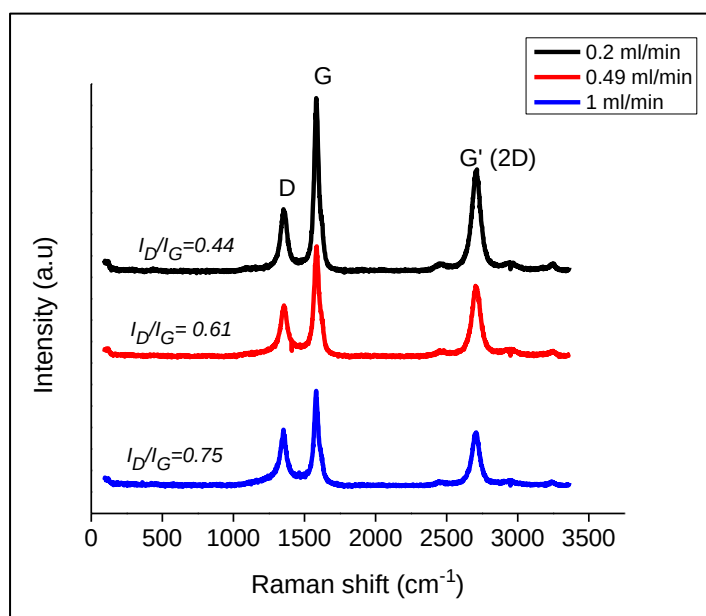


Figure 3.10: Raman spectra of CNTs made at varied injection rates

Figure 3.11 shows the XRD spectra of CNTs synthesized at varied injection rates. The characteristic (002) and (100) diffraction peaks of CNTs were observed at $2\theta = 26.3^\circ$ and $2\theta = 47.2^\circ$ respectively. At a lower injection rate of 0.2 ml/min the (004) peak was observed at $2\theta = 59.5^\circ$. The crystallinity of the CNTs was reduced as the precursor injection rate was increased, as indicated by the reduced sharpness of the peaks. This was also observed from the TEM and Raman results, where faster injection rates resulted in insufficient time for the synthesis of highly crystalline CNTs.

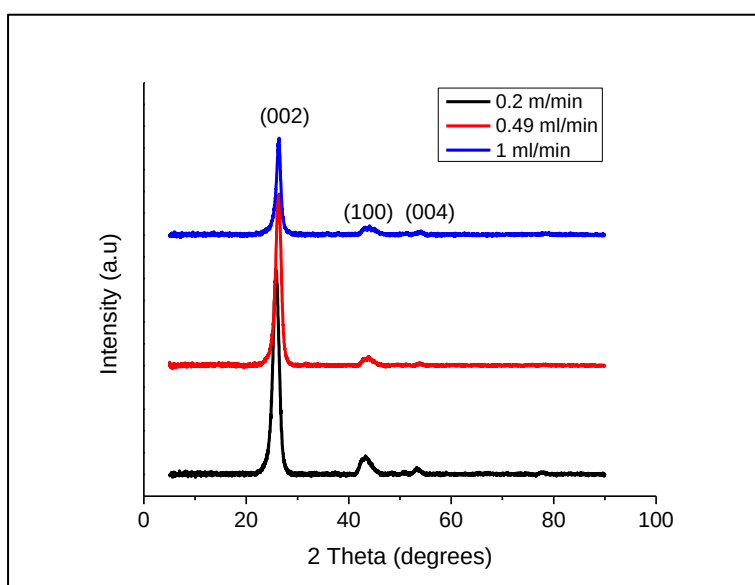


Figure 3.11: XRD spectra of CNTs at synthesized varied injection rates

3.2.3.3 Thermal analysis

In Figure 3.12, the TGA and derivative plots of MWCNTs synthesized at varied injection rates (0.2-1 ml/min) are presented. The oxidation temperatures were found to be 649, 628 and 610 $^\circ\text{C}$ at rates of 0.2, 0.49 and 1 ml/min respectively. The major weight loss was attributed to the decomposition of MWCNTs. A decrease in oxidation temperature with an increase in the injection rate was observed. The residual mass (due to Fe_2O_3) was observed for the CNTs synthesized at 0.2, 0.49 and 1 ml/min was 4.7%, 3.9 and 7.8% respectively.

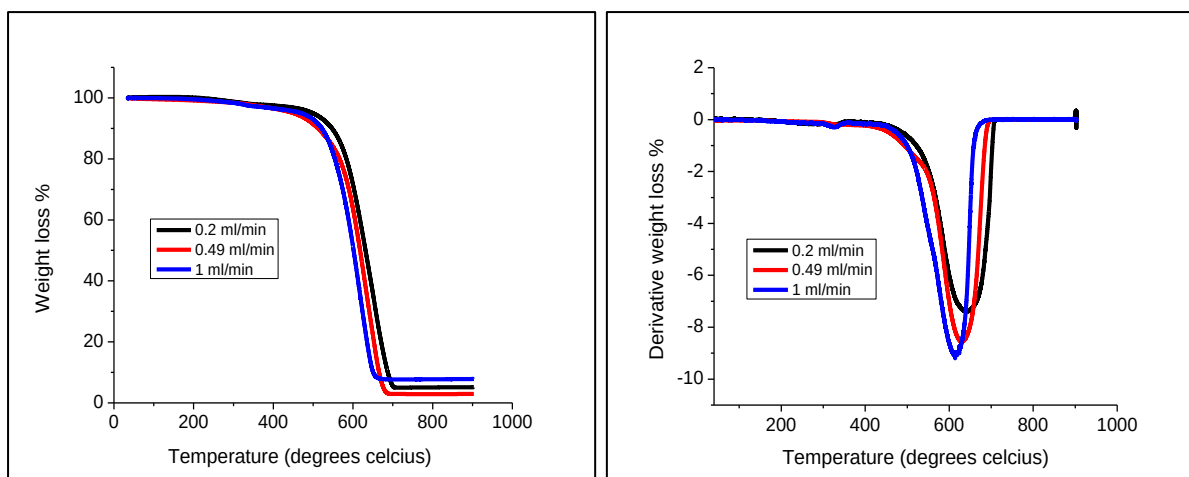


Figure 3.12: TGA and derivative plots synthesized at varied injection rates

3.2.4 Effect of flow rate

3.2.4.1 Morphology

A carrier gas (N_2) was used to deliver reactants into the reaction furnace and also to provide an inert environment to prevent the oxidation of the CNTs. In FCCVD synthesis, the most commonly used carrier gas is hydrogen or a mixture of hydrogen with argon or nitrogen [36]. In this study, the carrier gas was only N_2 to ensure a facile and economically viable method for industrial scale up. The temperature and injection rate were kept constant at 850 °C and 0.2 ml/min respectively. It has been noted that H_2 is responsible for producing CNTs of small diameters and improved yield and purity [36]. However, for this project wide CNTs are acceptable.

Abdullah et al., varied the Ar/H_2 ratio and found that H_2 at a flow rate of 600 ml/min provided an optimum yield of 97% CNTs with minimal amorphous carbon formation [37]. In this study, a low N_2 flow rate of 120 ml/min up to 160 ml/min was employed. At higher flow rates, above 120 ml/min, CNTs with a spiral/wavy shape were formed as shown in Figure 3.13. These morphologies are commonly observed in CNT bundles grown by CVD and have been attributed to oscillations in the gas flow [33]. An increase in the flow rate resulted in an increase in the amount of impurities (amorphous carbon), depicted by globules. This was attributed to the rapid N_2 flow which resulted in a decreased or insufficient residence time for CNT growth. The average diameter was reduced with an increase in carrier gas flow rate

from 83 to 47 nm. The number of large particles was also reduced, showing the advantage of making CNTs from smaller particle sizes at higher flow rates.

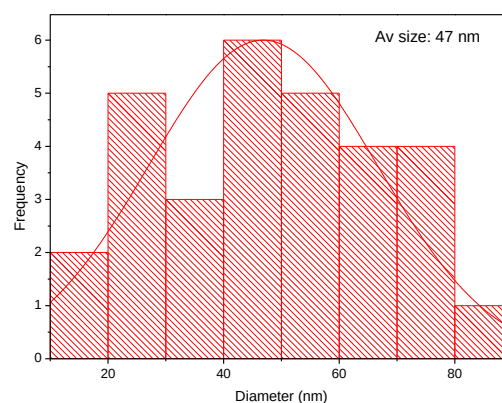
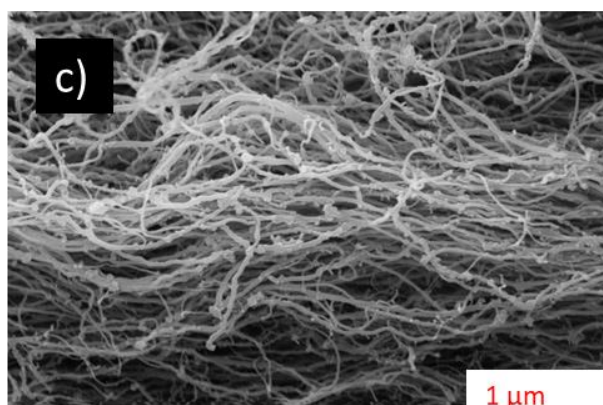
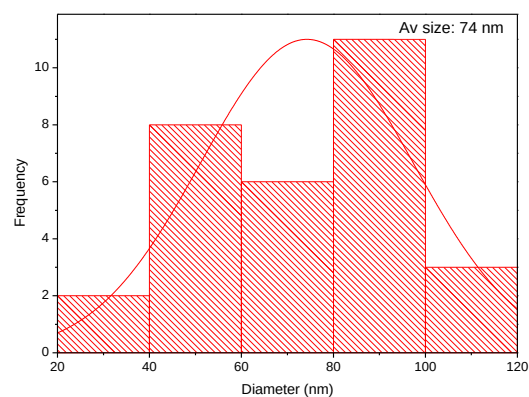
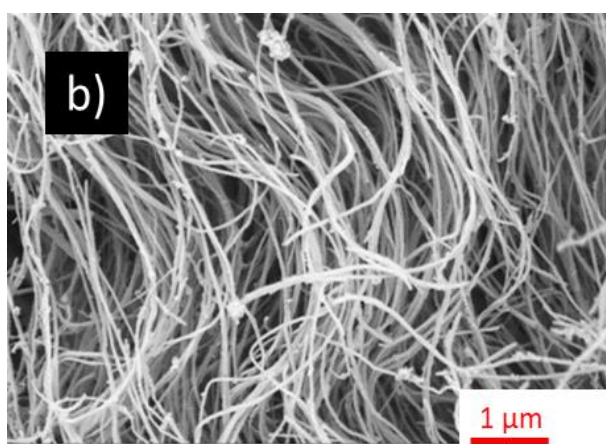
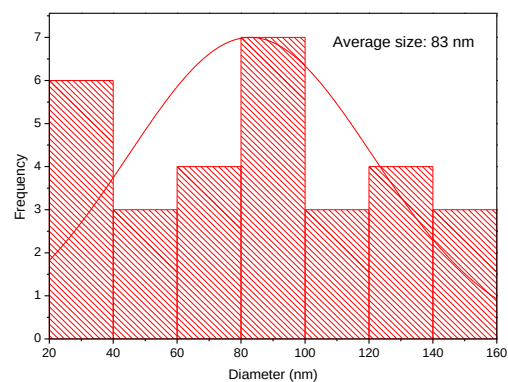
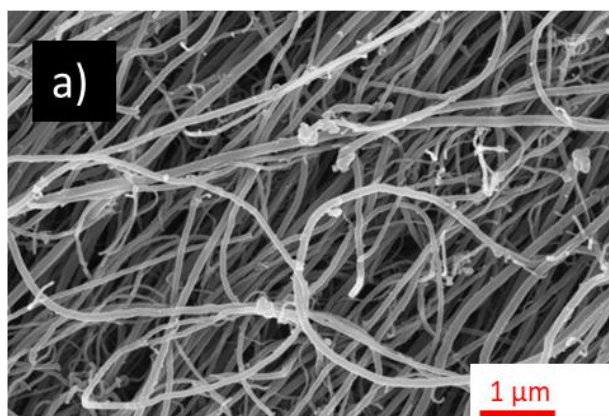


Figure 3.13: SEM images of CNTs and particle size distribution histograms at varied N₂ flow rate a) 120 ml/min, b) 140 ml/min and c) 160 ml/min

The TEM images in Figure 3.14 show hollow MWCNTs have been formed at the various N₂ flow rates. As the flow rate was increased, the crystallinity and purity of the CNTs was reduced. At 140 ml/min the MWCNTs were defected and amorphous carbon was formed. At 160 ml/min the CNTs were clustered and showed structural deformities. A decrease in the diameter of the CNTs at higher N₂ flow rate was observed which is consistent with other research findings [38]. The impurities shown by EDS were iron from the catalyst and copper from the grid. At flow rates of 140 and 160 ml/min silicon was also found as an impurity and this relates to removal of the CNTs by scraping of the glass CVD reactor.

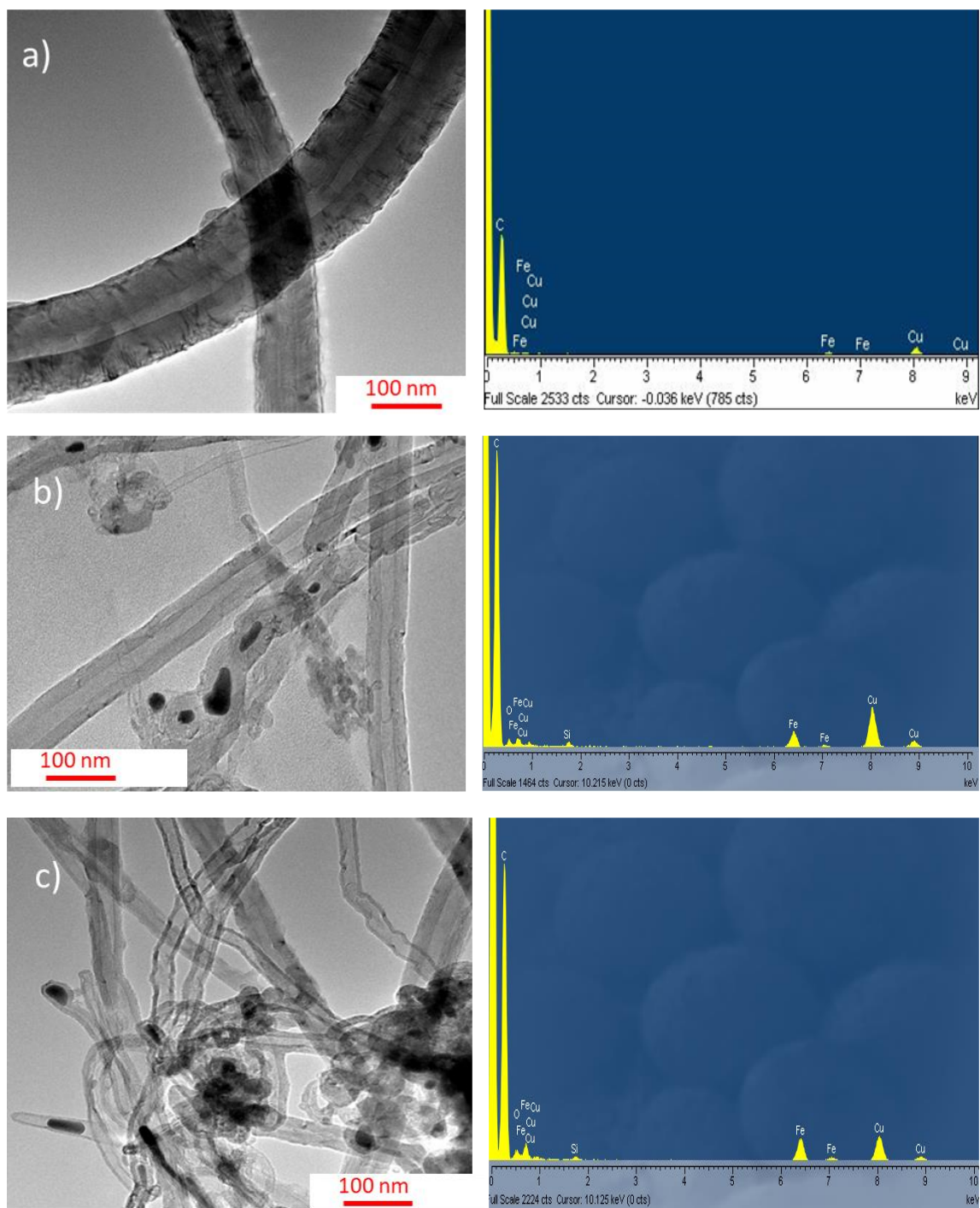


Figure 3.14: TEM images and EDS of CNTs synthesized at various N₂ flow rate a) 120 ml/min, b) 140 ml/min and c) 160 ml/min

3.2.4.2 Raman spectroscopy analysis

Figure 3.15 presents Raman spectra of MWCNTs synthesized at various carrier gas (N₂) flow rates. The crystallinity of the MWCNTs was reduced at the higher nitrogen flow rate. This was shown by an increase in the I_D/I_G ratio of 0.44, 0.54 and 0.57 for CNTs prepared at 120, 140

and 160 ml/min respectively. The TEM images in Figure 3.14 also show more defects and amorphous carbon as the flow rate was increased. Furthermore, the MWCNTs lost their alignment and started bundling-up. This was also observed by Abdullah et al., [37] where an increase in the carrier gas resulted in carbon impurities as clusters or unsuccessful growth of CNTs. The optimum flow rate was found to be 600 sccm (Ar-H₂ 100:500). However, at this flow rate, low quality CNTs were produced with an I_D/I_G ratio of 1.06 [37].

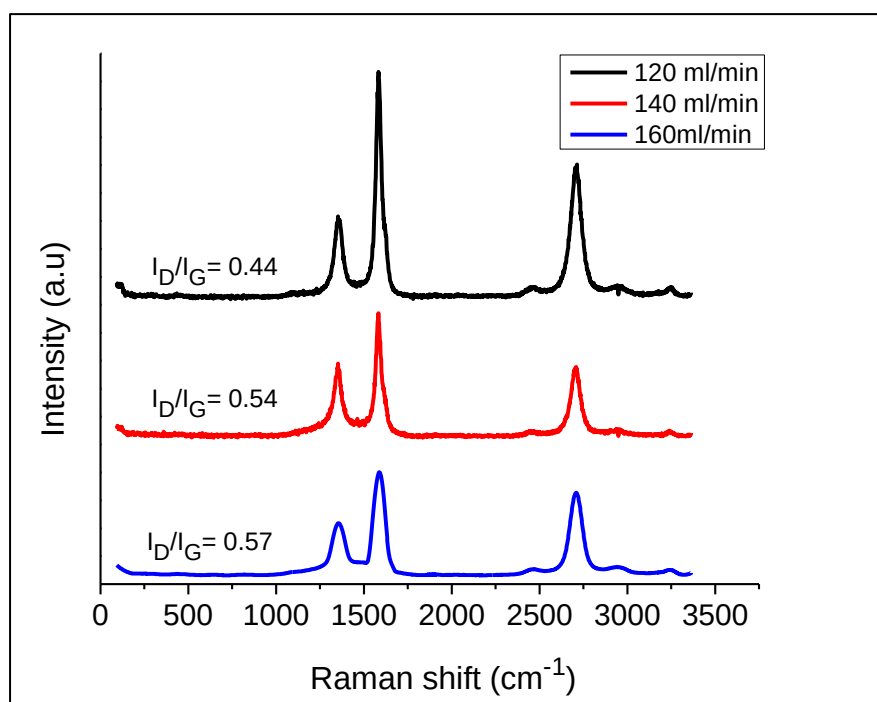


Figure 3.15: Raman spectra of MWCNTs synthesized at varied flow rate

In Figure 3.16, the XRD spectra of the CNTs synthesized at various flow rates is shown. The (002) and (100) diffraction peaks characteristic of CNTs were observed at $2\theta = 26.3^\circ$ and $2\theta = 47.2^\circ$ respectively. The (004) peak was only observed at a flow rate of 120 ml/min. The additional peak as well as the intensity and sharpness of the (002) peak were indicative of a high degree of crystallinity.

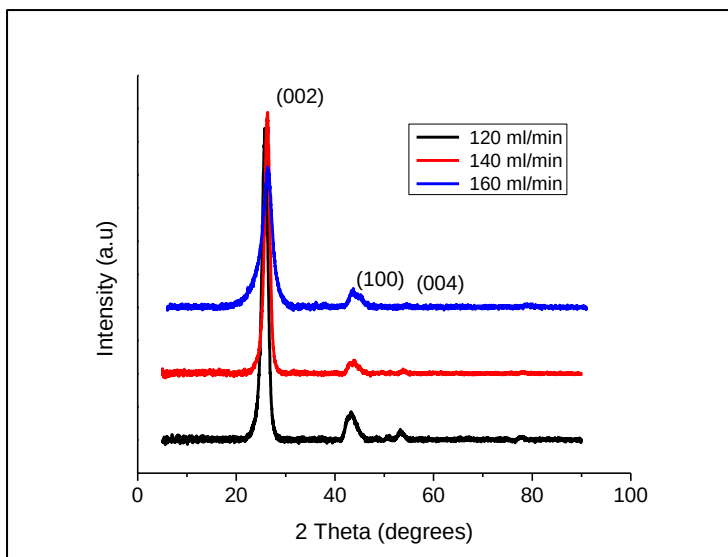


Figure 3.16: XRD spectra of CNTs synthesized at varied flow rates

In Figure 3.17, TGA and derivate plots at varied N_2 flow rates (120-160 ml/min) of the CNTs are presented. The oxidation temperatures were found to be 647, 631 and 620 °C for CNTs produced at the 120, 140 and 160 ml/min flow rates, respectively. It was shown that an increase in the flow rate reduced the crystallinity of the MWCNTs. The stability of all the synthesized MWCNTs was in the range of (620-650 °C) which was higher than those recorded using the CCVD method [39]. The MWCNTs synthesized at 100 ml/min had the lowest iron residual weight of 4.7% followed by 5.6 and 8.1 % for CNTs made at 120 and 140 ml/min flow rates, respectively.

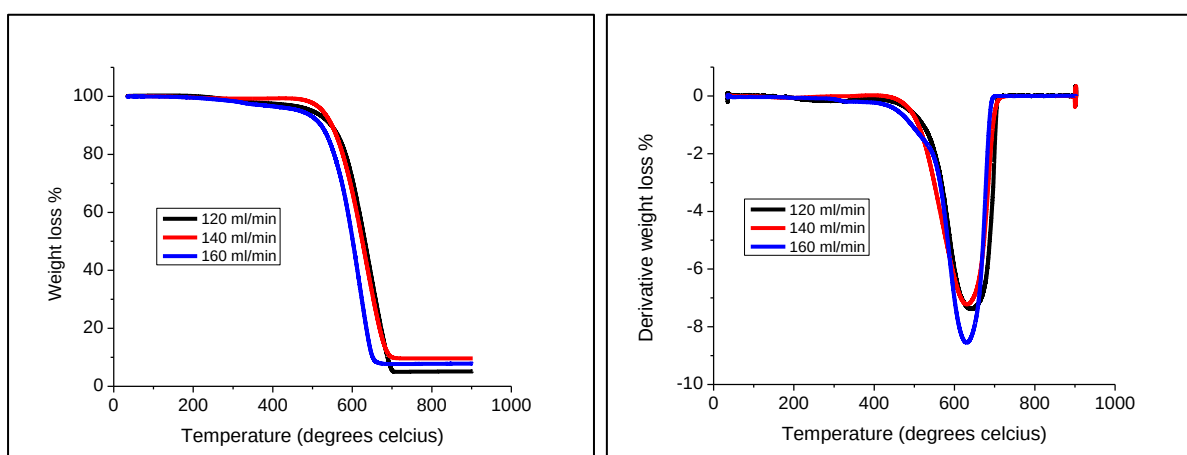


Figure 3.17: TGA and derivate plots of MWCNTs synthesized at varied flow rate

3.2.4.3 Functional group analysis

FTIR spectroscopy was used to study the structural changes caused by the modification of MWCNTs through acid treatment. The MWCNTs presented in the previous sections were functionalized/acid treated. This section shows the effect of functionalization by comparing the pristine and acid treated CNTs (as detailed in Chapter 2).

FTIR spectra of pristine and functionalized MWCNTs synthesized at optimum conditions of 850 °C, 120 ml/min N₂ flow rate and 0.2 ml/min precursor injection rate are represented by Figure 3.18. At around 3400 cm⁻¹, a peak was observed for the functionalized MWCNTs and assigned to O-H stretching. This was attributed to absorbed atmospheric moisture or oxidation during functionalization [40]. Dominant CH₂ stretches were observed at 2989 and 2900 cm⁻¹ for the functionalized CNTs and alkyl peaks were observed at ca. 2900 cm⁻¹ in both spectra. These were attributed to the backbone/framework of the CNTs. Upon functionalization, prominent hydroxyl peaks were observed at 1652, 1395, 1254 and 1058 cm⁻¹ which were distinctive absorption peaks for C=O and C-O stretching bands of carboxylic acid group [41]. The existence of these functional groups proved the successful functionalization of the MWCNTs. This was important for the intended application of CNTs in the brick composites. The hydroxyl groups have been found to improve the dispersion of the CNTs, thus, facilitating better interfacial interaction with the composite matrix. This ensures effective mechanical reinforcement of the composite.

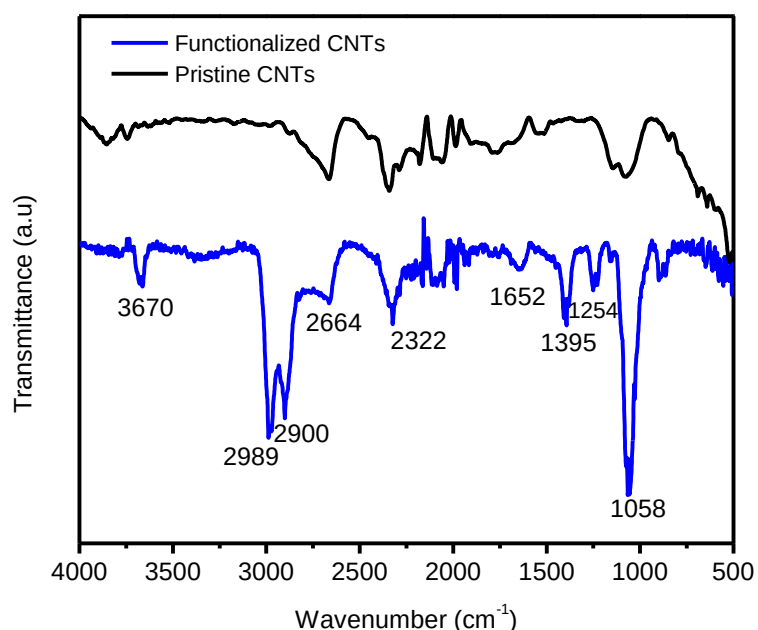


Figure 3.18: FTIR spectra of pristine and functionalized CNTs

3.2.4.4 Surface area

In Table 3.2, the BET surface area and pore volume of MWCNTs synthesized at various conditions is presented. Materials with the highest yield (Table 3.1) were chosen for the CNTs surface properties study. The pristine (as-synthesized) MWCNTs from optimum reaction conditions showed the lowest surface area and pore volume of $2.45 \text{ m}^2/\text{g}$ and $0.00307 \text{ cm}^3/\text{g}$ respectively. This was ascribed to the presence of the high amount of amorphous carbon produced, which is known to have a lower surface area than the CNTs. Furthermore, pristine MWCNTs tend to be more agglomerated/bundled due to the strong intermolecular forces which in turn affects their surface area. A great improvement in the surface area ($50.91 \text{ m}^2/\text{g}$) and pore volume ($0.1149 \text{ cm}^3/\text{g}$) following acid treatment functionalization was observed. The results were higher than those reported for MWCNTs ($36.0 \text{ m}^2/\text{g}$) treated using 30% HNO_3 [42]. The CNTs synthesized at a higher flow rate showed the second highest surface area and pore volume of $36.8 \text{ m}^2/\text{g}$ and $0.071 \text{ cm}^3/\text{g}$ respectively. Lastly, CNTs synthesized at a lower temperature and higher flow rate had the lowest surface area ($22.8 \text{ m}^2/\text{g}$) and pore volume ($0.061 \text{ cm}^3/\text{g}$).

Table 3.2: BET surface area and pore volume of MWCNTs synthesized at various conditions

Material	BET surface area (m ² /g)	Pore volume (cm ³ /g)
p-MWCNTs (850 °C, 0.2 ml/min, 120 ml/min)	2.45	0.0034
f-MWCNTs (850 °C, 0.2 ml/min, 120 ml/min)	50.9	0.110
f-MWCNTs (800 °C, 0.2 ml/min, 140 ml/min)	22.8	0.061
f-MWCNTs (850 °C, 0.2 ml/min, 160 ml/min)	36.8	0.071

*p-pristine, f-functionalized

3.2.5 Properties of importance of MWCNTs for application in brick composites

The application of CNTs in bricks has been of interest due to the properties CNTs impart to brick composites. The homogeneous dispersion of CNTs within the composite matrix is critical as inefficient dispersion can lead to weak spots, thus, compromising the strength of the composite [43]. In this study, the surfaces of the CNTs were functionalized by acid treatment to introduce polar functional groups. These are known to improve dispersion and thus, interfacial interactions within the matrix [44]. It was observed from the FTIR spectra (Figure 18) that the hydroxyl groups were successfully introduced on the surfaces of CNTs which will aid better dispersion within the composite. Inherently, CNTs possess high mechanical strength and as a result are used as a reinforcement material. The mechanical strength of CNTs is linked to their crystallinity. Highly crystalline CNTs tend to have higher mechanical strength because they contain minimal defects and impurities. Furthermore, the tensile strength of CNTs has been reported to reduce by up to 85 % due to high levels of defects [45]. An I_D/I_G ratio (which correlates to crystallinity) of 0.44 was obtained for the CNTs synthesized at optimum conditions. This showed relatively crystalline CNTs that are expected to improve the strength of the composites. The synthesized CNTs were long, with an average length of 414 μm , which is an important property for the bridging effect within the matrix of the composites to reduce microcracks [46]. Furthermore, CNTs are known to improve the thermal stability of composites and this influences the strength of the composites when exposed to various environmental conditions [43]. CNTs with a thermal stability of up to 649 °C were obtained. The improvement in the thermal stability of the composite can be ascribed to the hollow structure of MWCNTs that results in mass transport barrier effect. This is because the

high aspect ratio of CNTs can increase the intricate path within the composite. Thus, delaying or blocking the transfer of the decomposition products in the composite [47]. Furthermore, the thermal stability of the polymer composite is improved by the interaction between the MWCNTs and the polymer chain. As well as the absorption effect of the free radicals by MWCNTs produced during decomposition [48].

3.2 Conclusion

This study was undertaken to provide a simple laboratory method to make MWCNTs. Many studies have been reported on making MWCNTs. In this study the focus was on using affordable and safe reactants and to optimize the yield and purity of the MWCNTs. Thus, nitrogen was used as a carrier gas, toluene as the carbon source, and ferrocene as the catalyst (and carbon source). The MWCNTs were successfully synthesized using a facile FCCVD method, without a promoter. The effect of the synthesis temperature, precursor injection rate and carrier gas flow rate were correlated with the quality and yield of the CNTs produced. It was observed that an increase in temperature increased the crystallinity and diameter of the MWCNTs. An increase in injection rate and flow rate had an inverse effect on the quality and yield of the MWCNTs. These are the expected and predicted results thus indicating confidence in the process used. The optimum synthesis conditions used to make the CNTs were found to be 850 °C, 120 ml/min N₂ flow rate and 0.2 ml/min precursor injection rate. Using these conditions, a carbon yield of 73% was obtained with the MWCNTs having an average diameter of 83 nm and length of 414 μm, an I_D/I_G ratio of 0.44, an oxidation temperature of 649 °C, and a purity of 94 %. The surface area was found to be 50.9 m²/g. The properties of CNTs required for application are high crystallinity which will result in high mechanical strength as well as enhance the thermal stability of the composite. Furthermore, the CNT's high aspect ratio will hinder microcrack formation in the composite. The results obtained suggests that the MWCNTs would be appropriate for application as a reinforcement material in brick composites.

3.3 References

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CHAPTER 4

CHARACTERIZATION OF RAW MATERIALS: COAL FLY ASH (CFA), COAL BOTTOM ASH (CBA) AND LOW-DENSITY POLYETHYLENE (LDPE)

4. Introduction

The repurposing of waste has gained popularity in many fields [1]. This has allowed waste to be viewed as a resource and has birthed several innovative solutions. It is crucial to understand the properties of the waste materials prior to their application. Thus, characterization, analysis and testing of the waste raw materials must be undertaken. This allows the utilization of the waste within its limit, without compromising the quality and standards of the product it is applied in. Coal fly ash (CFA), coal bottom ash (CBA) and low-density polyethylene (LDPE) are waste products generated in high volumes [2,3]. Hence, considerable research is focused on their beneficiation to achieve a circular economy. The building and construction industry in particular, has taken efforts of incorporating the waste in some composites [4–6]. This has reduced the dependency on natural resources such as sand and stone by their partial replacement with waste materials [7].

In a typical plant, CFA is carried in the flue gas as it exits the combustion chamber and collected mechanically, by electrostatic precipitators or bag houses [8]. It consists of small glassy particles derived from minerals present in coal [9]. The particle size is usually in the range of 0.5-200 microns [10]. The composition and properties of CFA differs according to the parent coal it was produced from, and the combustion conditions. Its composition is a complex mixture of amorphous and crystalline phases, with alumina (Al_2O_3), silica (SiO_2) and iron oxides present as major constituents as well as other elements such as copper, sulfur and magnesium in various amounts [11]. The particles of CFA have a layered structure as a result of successive deposition of several chemical species, as the temperature decrease along the particle's path in the furnace. In the core of the CFA, remains the crystalline phases such as mullite and quartz, while the glass phase of aluminosilicate covers the surface of the particles [12].

Similar to CFA, coal bottom ash (CBA) is a coal combustion residue generated by thermal power plants. However, instead of being carried in the flue gas, it settles at the bottom of the

combustion furnace [13]. CBA accounts for about 20% of the combustion residue and the rest is CFA [13]. It is lighter, porous, coarser and consists of particles $>100\text{ }\mu\text{m}$. While its density ranges from $1200\text{ to }1620\text{ kg m}^{-3}$, it is lower than that of CFA ($1900\text{ to }2800\text{ kg m}^{-3}$). The particle size distribution of CBA is similar to that of fine aggregates. Thus, it has been used to replace fine aggregates in concrete [14]. It has a mineral composition comparable to that of CFA with aluminosilicates as the major constituents. However, it has a higher content of unburnt carbon and can be promoted to carbonaceous material [14].

Low density polyethylene (LDPE) waste is the most abundant plastic waste worldwide and a major contributor of land pollution and ecological unsustainability [15]. The waste accumulates at a fast rate because most LDPE plastics are single-use and are not effectively recycled. LDPE is a thermoplastic polymer with C-C, C-H bonds, and a density of 0.92 g/cm^3 , melting point of $105\text{-}115\text{ }^{\circ}\text{C}$ and tensile strength of $0.2\text{-}0.4\text{ MPa}$ [16]. The physical properties of waste LDPE may vary to those of the pristine polymer according to the recycling processes it underwent. Plastic recycling is typically performed *via* four techniques; i.e., primary (closed-loop), secondary (through mechanical processes), tertiary using chemicals and energy recovery which involves incineration. There is currently a heavy reliance on primary techniques which require almost-pristine plastics [17]. Polymers reprocessed by melt and remoulding have lower molecular weights, less mechanical strength, and reduced thermal stability compared to virgin materials [18]. Thus, limiting their application in composites such as building materials as strength is of importance in such materials. However, studies have been conducted on the types of recycled plastics that can be applied in building materials and the maximum loading in various composites to ensure the required quality is maintained [19]. Furthermore, the incorporation of plastics offers the advantage of lightweight materials as their density is far below that of concrete [15]. Notably, light weight building materials are attractive in many sectors and have a direct impact on cost savings.

The building and construction industry is the major consumer of CFA and CBA [20]. It has set standards on the type and quality of coal ash that can be employed [21]. It has been noted that in cement composites, coal ash with high LOI tend to require high amounts of water during preparation, results in poor air entrainment, segregation and also compromises the ultimate compressive strength and quality of the mixed components [22].

The mineralogical analysis using techniques such as X-ray fluorescence spectroscopy (XRF) and energy dispersive spectroscopy (EDS) is the primary test used to identify the elemental composition in CFA and CBA. For application in building materials, the qualitative and quantitative elemental composition analysis is important for understanding potential leachability. The metals in coal ash can pose a threat to both the exposed human beings and the environment. Thus, their leachability must fall within a set threshold limit. Furthermore, analytical techniques such as inductively coupled plasma mass spectrometry/ optical emission spectroscopy (ICP-MS/OES), atomic absorption spectrometry (AAS), differential pulse anodic stripping voltammetry (DPASV) are also used for elemental composition analysis and have the advantage of low detection limits [23].

Other techniques of importance are XRD, which gives crystallographic information, SEM used for morphological analysis, FTIR for functional group determination and TGA for thermal stability [24]. The TGA analysis is paramount especially for LDPE as it is known to have a high linear burning rate. Thus, its incorporation in composites must be within limits to ensure the required thermal stability is maintained.

4.1 Experimental

The CFA and CBA used in this project was supplied by Lethabo thermal power plant (Free State, South Africa) (Figure 4.1). At the Lethabo Power Plant, ash is deposited as a dry residue. The coarse ash and fine ash are deposited as a mixture on to the ash dump and fly ash is collected from the combustion chamber. The CFA and CBA were used as-received without any treatment or purification (Figure 4.2 a) and b)). They were kept in a tightly sealed container and kept away from light to ensure their composition is not altered prior to characterization.

LDPE was collected from Whole Earth, a plastic recycling company. It was already sorted and cleaned upon receipt. The waste plastics were air-dried and cut to small sizes for easier application (Figure 4.2 c)). The waste materials were characterized using various techniques to study their properties for application in building composites.



Figure 4. 1: Image of Lethabo thermal power plant ash collection sites.



Figure 4.2: As received a) coal fly ash, b) coal bottom ash, and c) low density polyethylene.

4.2 Results and discussion

4.2.1 Coal fly ash

4.2.1.1 Physical properties of coal fly ash

Table 4.1 presents the physical properties of CFA. The average particle size of CFA was 36.6 μm with the majority of the particles below 10 μm . The particles were within the 0.5 μm -300 μm reported particle size range [20]. Furthermore, Lethabo Power Plant CFA has been

identified as fine with 90% of its particles below 11 μm [21]. The particle size of CFA is important in its application as a filler in composites. Smaller particles normally result in denser and compact composites as they can fill small spaces [22]. The true density was 2.4 g/cm^3 and the pH readings showed that the CFA was basic (11.1) which was as a result of the Ca (present as CaO) in high concentrations of 7.03% (Table 4.2).

Table 4.1: Physical properties of coal fly ash

Average particle size (μm)	True Density (g/cm^3)	pH
36.6	2.4 $\pm$ 0.03	11.1

4.2.1.2 Mineralogical analysis

Table 4.2 shows the ICP-OES elemental composition of CFA. The major constituents were Si, Al, Ca and Fe existing as metal oxides, accounting for about 87% of the total composition. While other minor oxides such as Cr, Mg and Ti accounted for almost 4%. Elements such As, Cd, Co, Cu, Mn, Mo, Ni, Pb, V and Zn were present in trace amounts (ppm). Cu and Pb were found to exceed the total concentration threshold (TCT0) limit in waste which is 16 and 20 ppm respectively [25]. However, they can only pose a health or environmental threat if their leachability is about the accepted threshold limit. The sum of SiO_2 , Al_2O_3 , Fe_2O_3 was found to be greater than 70%, meaning that the CFA could be classified as Class F according to the ASTM. This type of fly ash has been used for cement replacement in building composites. The LOI was 1.91%, which represented the amount of unburnt carbon. This was comparable to the 2.4% obtained from TGA (Figure 5). The LOI was within the specified requirement of <6% by the ASTM for building materials. The Si/Al ratio was found to be 1.7, this ratio has been found to influence the compressive strength of geopolymers from fly ash. It has been reported that the higher the ratio the higher the compressive strength. In some instances, Si is introduced as an additive to improve the compressive strength [26].

Table 4.2: ICP analysis of coal fly ash

Sample name	Al ₂ O ₃ %	CaO %	Cr ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	SiO ₂ %	TiO ₂ %	LOI %		
Coal fly ash	28,5	7,03	0,131	3,5	1,84	48,4	1,55	1,91		
	As ppm	Cd ppm	Co ppm	Cu ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	V ppm	Zn ppm
	<10	<10	18,74	66,21	255,86	<10	54,42	39,06	138,22	36,42

4.2.1.3 Crystallographic analysis

The X-ray diffractogram of CFA shown in Figure 4.3, presents crystalline phases of quartz (SiO₂), mullite (Al₆O₁₃Si₂) and hematite (α -Fe₂O₃). The hematite phase is not abundant in the CFA, which might be the reason Fe was not detected in the EDS. The quartz and mullite phases were dominant, accounting for their abundance in the sample, which resulted in the formation of the glassy smooth surface of CFA, which is dense and chemically stable [27]. Quartz came from the inorganic part of the coal and did not merge during the combustion process [28]. While, mullite was formed from the coal combustion process. Mullite is not reactive, and found in Class F fly ash and the class was confirmed by ICP. However, quartz is present in all types of fly ash. The presence of an amorphous phase was indicated by the broad hump between the $2\theta=15-35^\circ$ region. This was observed in other studies and attributed to aluminosilicate glass [28]. The dominance of the aluminosilicate glass phase in both amorphous and crystalline phase (mullite) was mainly attributed to rapid cooling of CFA after the coal combustion at high temperature [29]. Aluminosilicate glass is formed from low calcium coal, while calcium aluminosilicate glass is formed from high calcium coal [30]. In CFA Class C, the latter is thought to be a reactive phase, which contributes to its higher reactivity than in Class F [30].

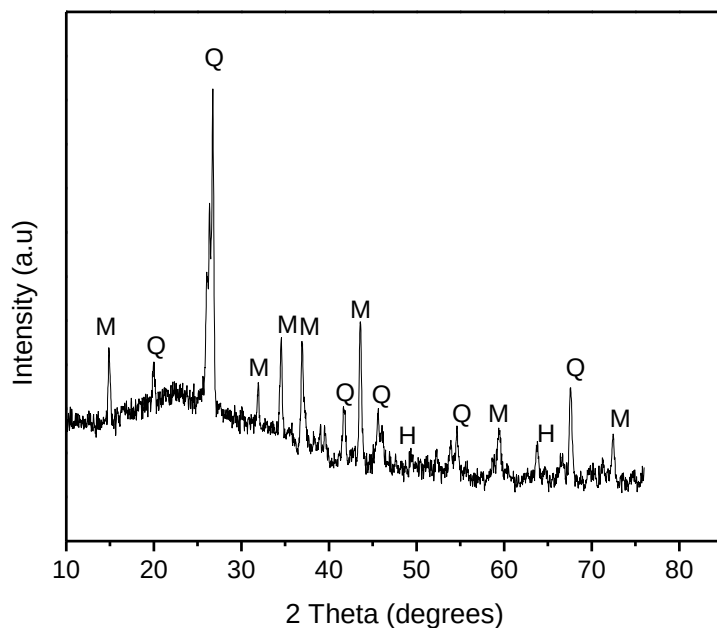


Figure 4.3: XRD profile of coal fly ash.

4.2.1.4 Morphological analysis

The majority of the as-received Lethabo thermal power plant CFA particles were spherical and smooth with smaller spheres on the surfaces of the larger ones as shown by SEM images in Figure 4.4. The coal combustion conditions such as the kindling temperature of coal and the rate of cooling informs the morphology of the CFA [31]. During the combustion process, minerals present in coal tend to behave like liquid before they solidify. They may decompose, fuse, oxidize, dissolve or aggravate to produce various morphologies of the CFA particles [31]. Notably, CFA particles solidify while suspended in the flue gases and tend to have spherical morphologies. Furthermore, spherical morphologies can be attributed to high silicon contents in the CFA [9], which was indeed observed from the XRD and EDS results. The spherical shape is also suggestive of moulded particles formed as a result of coagulation, condensation and nucleation during high temperature combustion [32]

The smooth surface of the particles is as a result of being covered with an amorphous glass phase [33]. It was observed from the EDS that the CFA had a high mineral content of Si, Al, O, Ca, K, Mg and trace elements of V and Mn. The spherical particles were below 10 micron (0.3-8 micron). As also shown by the EDS, the spherical particles were mainly made up of aluminosilates (Al, Si and O). Larger particles with an average of 20 micron were also

observed, with irregular shapes and rougher surfaces. The rectangular shaped particles were detected by EDS to be mainly carbon with the presence of Al and Si which was expected as they are the major constituents in the sample. During the combustion process of coal, carbon is burnt. However, as shown with this fly ash, residual unburnt carbon remained. This was also shown with the LOI obtained from analysis, which gives an indication of the residual carbon.

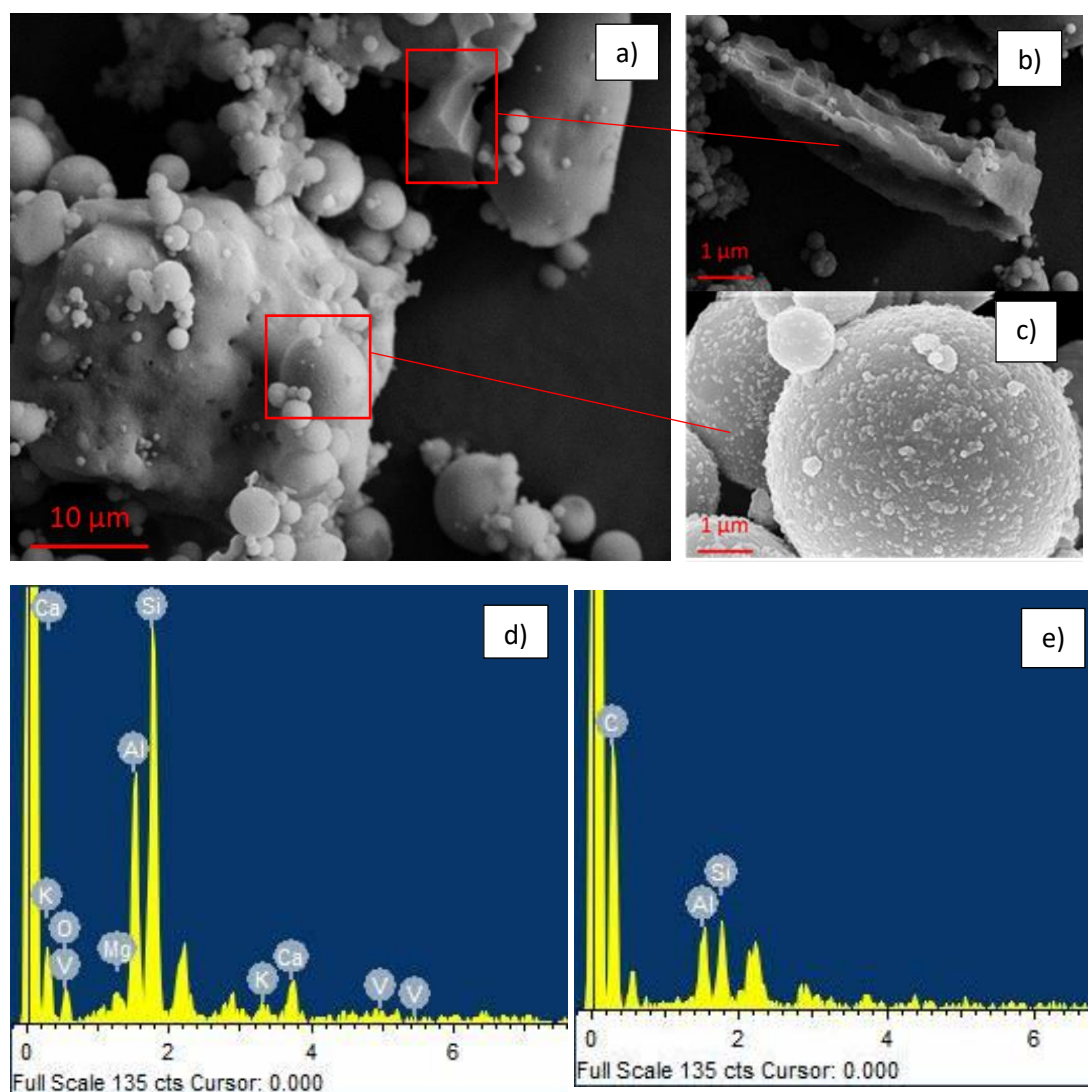


Figure 4.4: SEM images and EDS spectra of coal fly ash.

4.2.1.5 Functional groups analysis

In Figure 4.5, an FTIR spectra of CFA is represented. A small peak around 3679 cm^{-1} was observed and attributed to hydroxyl groups of water molecules adsorbed on the surface of

the CFA and silanols ($\equiv\text{Si}-\text{OH}$) [9]. CH_2 stretch was observed at 2986 and 2898 cm^{-1} and at 1404 cm^{-1} a peak ascribed to C-O stretch was shown. The prominent CFA asymmetrical stretching mode associated with T-O-T stretching (T= Al, Si) was detected at 1062 cm^{-1} wavenumber [34]. This stretching mode was observed with materials such as CFA whose major components are Al and Si (aluminosilicates) as also shown in the XRF, EDS and XRD spectra. The shoulder peak observed at 901 cm^{-1} and the subsequent peak at 778 cm^{-1} forming part of the broad band, were ascribed to the presence of the glassy phase in the CFA [35]. The glassy phase was also depicted in the SEM images as accounting for the smooth surface of the spherical CFA particles. At 550 cm^{-1} an Al-O bend was observed which represented the octahedral aluminium present in the mullite ($\text{Al}_6\text{O}_{13}\text{Si}_2$) phase. Further at 440 cm^{-1} a T-O (T=Al, Si) bending vibration was observed [36].

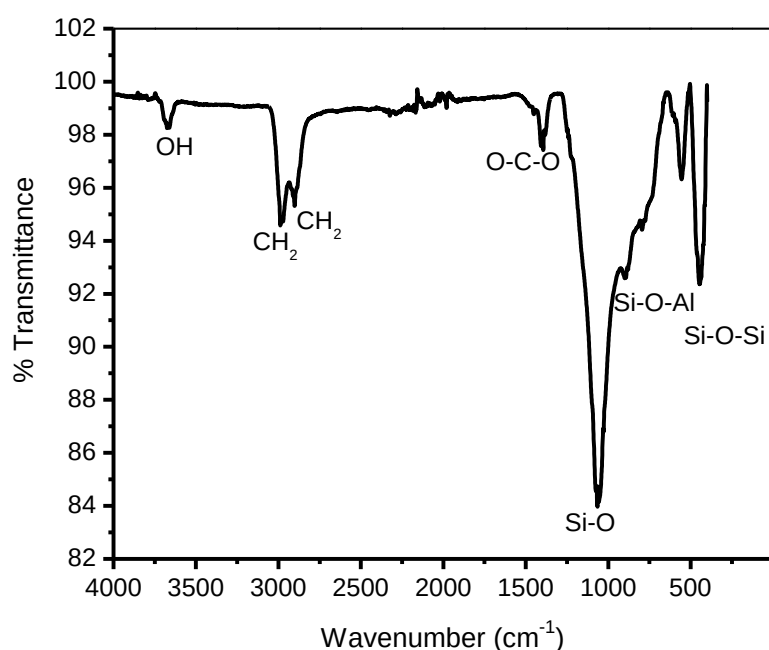


Figure 4.5: FTIR spectrum of coal fly ash.

4.2.1.6 Thermal analysis

TGA and derivative plots are shown in Figure 4.6 under an oxygen environment. As shown in the plots, CFA was thermally stable even at high temperature because its major constituents are minerals. The weight loss observed below $200\text{ }^{\circ}\text{C}$ was attributed to the loss of atmosphere

moisture absorbed by the sample. The residual carbon which was observed on the ICP-OES as loss on ignition (LOI) decomposed above 200 °C. Furthermore, the weight loss that occurred between 400 °C and 680 °C, was attributed to the decomposition of volatile organic compounds and the dehydroxylation due to the loss of water as a result of condensation of silanol groups forming siloxane bonds [37]. The presence of silanols was also observed on the FTIR (Figure 4.4). The mass loss is below 3% even above 800 °C, which shows that CFA is thermally stable as the major constituents are metals. Thus, CFA can be used as a filler to stabilize polymer composites.

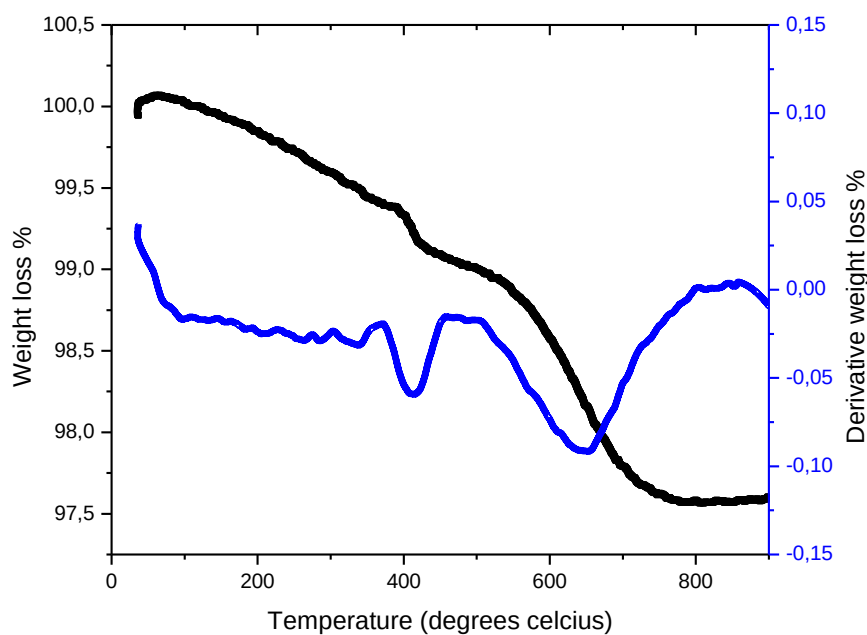


Figure 4.6: TGA and derivative plots of coal fly ash.

4.2.2 Coal Bottom Ash

4.2.2.1 Physical properties of coal bottom ash

The physical tests performed on CBA are reported in Table 4.3. The average particle size of CBA was found to be 58 μm , which was larger than that of CFA. This was as a result of the larger particles that settled at the bottom of the chamber where CBA was collected. However, the particle size of the CBA was lower than the reported particle size of 180-1000 μm . This is because the CBA collected from the Eskom power plant was processed prior to its release to

ensure safer disposal. Thus, the CBA collected and used in application was of a finer particle size. The true density was 2.3 g/cm³ which was similar to that of CFA as well as that reported in literature [36]. The pH was 10.3 and classified as mildly alkaline [37]. The pH was lower than that of CFA due to the lower level of Ca (4.64%) compared to 7.03% in CFA.

Table 4.3: Physical properties of coal bottom ash

Average particle size (μm)	True Density (g/cm ³)	pH
58	2.3 ±0.1	10.3

4.2.2.2 Mineralogical analysis

Table 4.4 presents an elemental analysis of CBA. SiO₂ was found to be the most abundant element at 53.3%, which was higher than in CFA (48.4%), followed by Al₂O₃, CaO and Fe₂O₃. Other metal oxide such as MgO, TiO₂ and Cr₂O₃ were found in smaller quantities respectively. Trace amounts of As, Cd, Co, Cu, Mn, Mo, Ni, Pb, V, Zn were observed similar to CFA. Unlike in CFA, in the CBA sample, Cu, Pb and also V were above the total concentration threshold (TCT0) limit which is 16, 20 and 150 ppm respectively, which can pose a risk if they leach above the acceptable limit [25]. The CFA and CBA were collected from the same power plant (Lethabo) and similarities in their elemental composition was expected. The LOI for the CBA was found to be 1.32% which was lower than that in CFA which was not expected. Unburnt carbon is usually higher in CBA than in CFA due to its larger particles that settle more at the bottom of the furnace rather than travel with the flue gas and collected as CFA. However, in both ash samples the LOI was low and fell within the <6% recommended limit for application in building composites. The Si/Al of CBA was found to be 1.9. This was slightly higher than CFA, which might result in stronger bricks than those produced from CFA.

Table 4.4: ICP-OES analysis of coal bottom ash

Sample name	Al ₂ O ₃ %	CaO %	Cr ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	SiO ₂ %	TiO ₂ %	LOI %		
Coal bottom ash	28,4	4,34	0,146	3,83	1,03	53,3	1,4	1,32		
	As ppm	Cd ppm	Co ppm	Cu ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	V ppm	Zn ppm
	<10	<10	17,79	59,17	245,12	<10	63,12	40,93	150,18	57,89

4.2.2.3 Crystallographic analysis

In Figure 4.7, an XRD profile of CBA is shown. The dominant crystalline phases were quartz (SiO₂) and mullite (Al₂O₃), which was also evident with the ICP-OES and EDS results. Minor phases of hematite (α -Fe₂O₃) were also observed similar to the CFA sample. CBA showed more crystalline quartz phase compared to CFA which had amorphous quartz (represented by the broad hump) also observed in another study [38]. Furthermore, the anorthite phase (CaAl₂Si₂O₈) was detected at $2\theta = 33^\circ$ for CBA which was not visible with CFA due to the amorphous vitreous components.

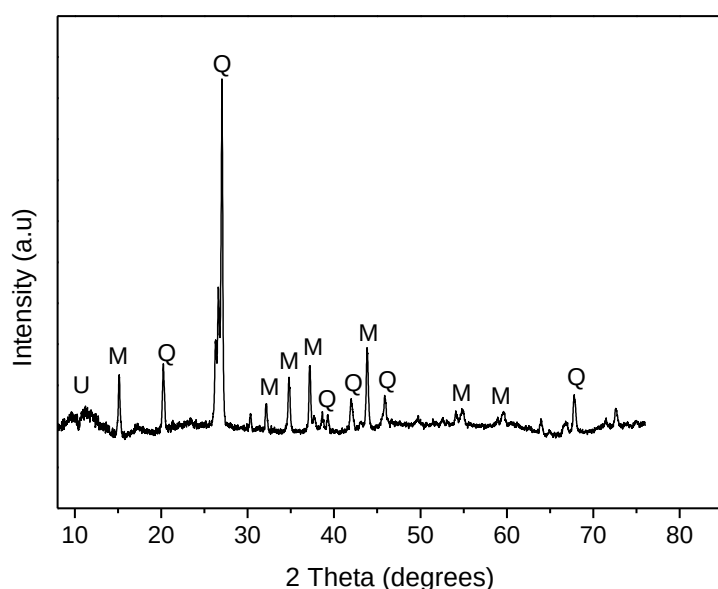


Figure 4.7: XRD profile of coal bottom ash.

4.2.2.4 Morphological analysis

The microstructure and particle size of CBA are influenced by the combustion temperature and cooling rate during the incineration process [39]. Figure 4.8 presents SEM images and EDS spectra of as-received bottom ash at different areas within the sample. The particles were spherical, cenospheres (hollow spheres filled with other smaller spheres) and irregular. They possessed a large size distribution (0.1-90 micron) with some very small spheres and large irregular particles. Agglomerated particles were also observed and have been found to be in the form of polycrystalline (formed during cooling), amorphous and glassy phases. The major elements which were detected by EDS were silicon (Si), aluminium (Al), calcium (Ca), iron (Fe) and these exist as oxides in the CBA [40]. Trace elements such as calcium, titanium, magnesium, potassium and phosphorus were also detected. Furthermore, there was gold (Au), palladium (Pd) which were the coating materials used and also carbon which was both from the carbon tape and a residue from the CBA. The residual carbon similar to CFA was detected by EDS to be the irregular rectangle shaped particles and attributed to incomplete combustion of the coal during incineration.

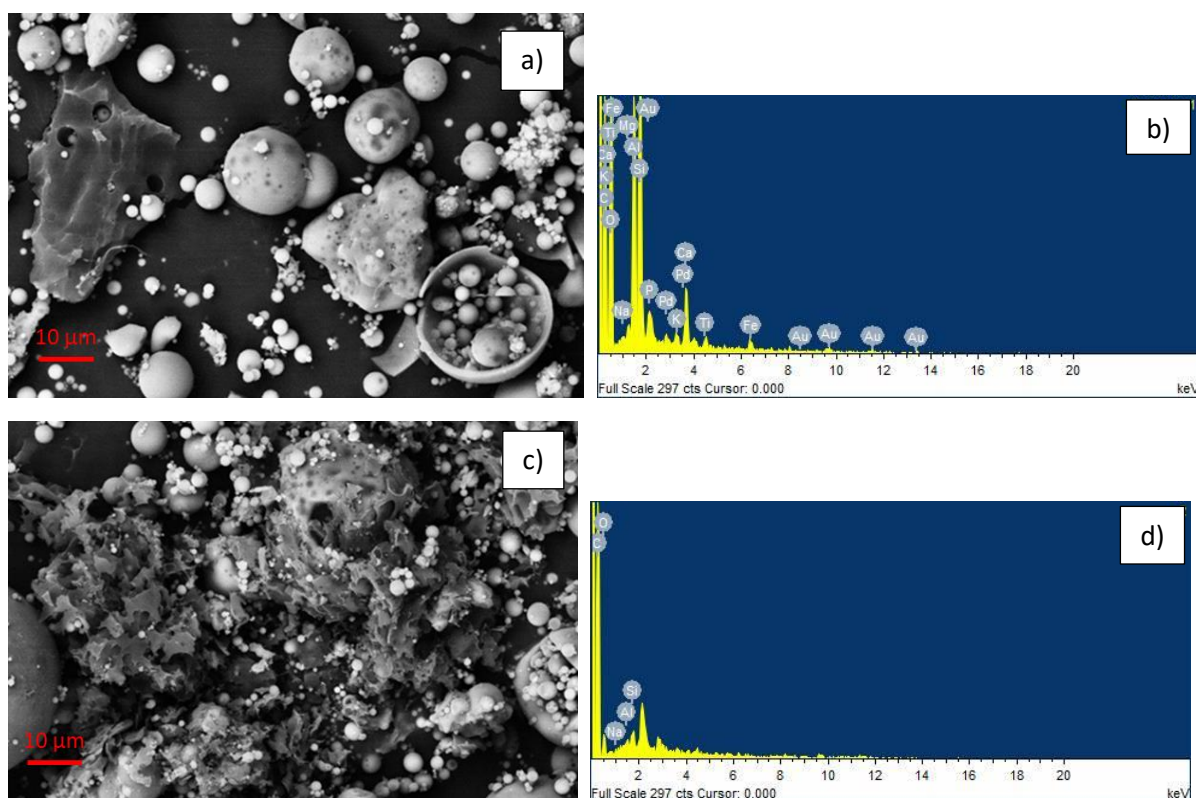


Figure 4.8: Images and EDS spectra of coal bottom ash.

4.2.2.5 Functional groups analysis

Figure 4.9 presents an FTIR spectrum of CBA. The spectrum is similar (with minor wavenumber shifts) to that of CFA (Figure 4.5), indicating that the samples were collected from the same power plant and potentially originates from the same or similar parent coal. The peak at 3680 cm^{-1} was attributed to the presence of hydroxyl groups due to surface moisture on the sample [41]. The two peaks at 2972 cm^{-1} and 2892 cm^{-1} were ascribed to CH_2 strength and at 1394 cm^{-1} a CO stretch was observed [42]. Several mineral oxide peaks were observed which corresponds with the ICP-OES results that showed most elements in CBA to exist as oxides. A prominent peak distinctive of aluminosilicates was observed at 1058 cm^{-1} which represented T-O-T (T= Si/Al) stretch. The shoulder peaks that accompanied this peak shown at 898 cm^{-1} was indicative of a glassy phase of the CBA. At lower wavenumbers bending modes of Al- and T-O were shown at 564 cm^{-1} and 457 cm^{-1} respectively [43].

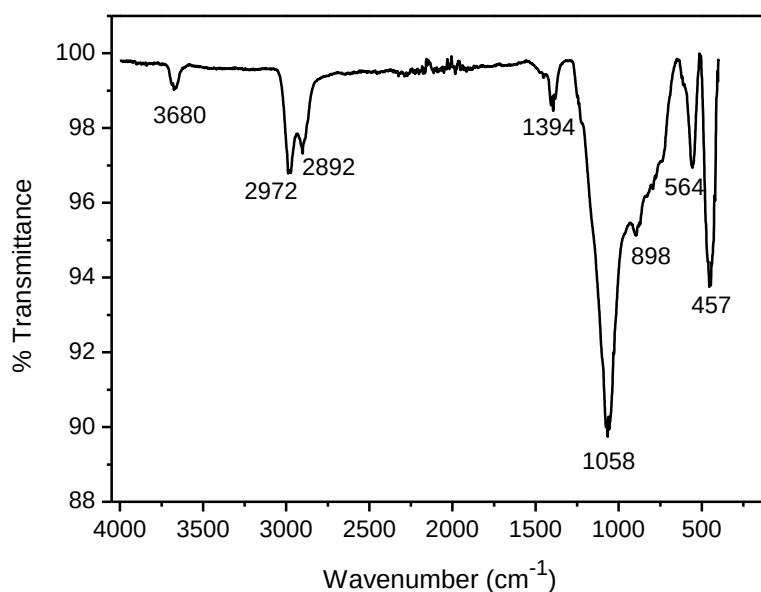


Figure 4.9: FTIR spectrum of coal bottom ash

4.2.2.6 Thermal analysis

Thermal decomposition peaks and weight loss at respective temperatures are shown in Figure 4.10. The initial weight loss below 200 $^{\circ}\text{C}$ was attributed to the loss of surface moisture. At

400 °C, a mass loss ascribed to dehydroxylation of C-H bond was observed. The major weight loss was observed at 650 °C and was attributed to the decarbonization of C-C bond which is a property of importance in the cement industry [44]. This type of CBA with low carbon content can be easily mixed with hydroxides to form cementitious products. A total weight loss of 2.2% was obtained, which was comparable to the LOI. The difference in the mass loss percentage is because LOI only accounts for the weight loss of unburnt carbon, while TGA accounts for the loss of other volatile compounds within the BA sample. The CBA was thermally stable at temperatures below 600 °C and thus, can play a vital role as a flame-retardant filler in polymer-based building composites.

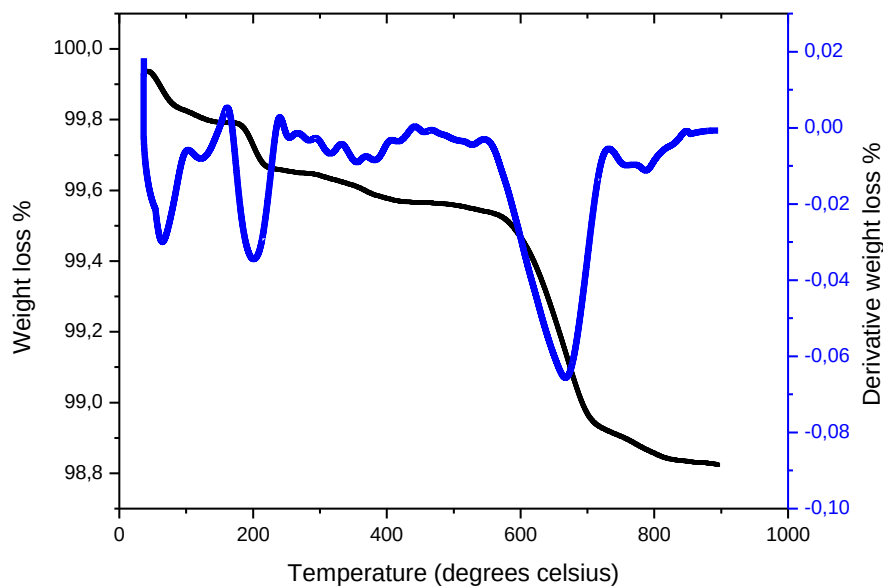


Figure 4.10: TGA and derivative plot of coal bottom ash.

4.2.3 Comparison of CFA and CBA

Table 4.5 shows the differences in properties of CFA and CBA. The ash samples had comparable properties as they were from the same power plant. However, some properties were different due to the residues being collected from different components of the combustion process. The properties of the ashes and their availability informed the type of ash that was used in application for this study. The LOI is an important property for application of coal ash in cement composites. However, in this study it did not play a significant role as cement was not used, thus, the hydration mechanism did not form part of the brick

development. The level of trace heavy metals which have a potential of being toxic when leaked was important. Furthermore, the thermal stability of the ashes was important as plastics which are flammable were used in the bricks. CFA had a lower thermal stability compared to CBA due to the higher levels of unburnt carbon present as also shown by the high LOI. However, it was not significantly lower than that of CBA and carbon nanotubes were applied in the composites to further improve the thermal stability of the composite.

Table 4.5: Differences in the properties of coal fly ash and coal bottom ash

Coal fly ash	Coal bottom ash
Lower level of SiO ₂ (48.2%)	Higher level of SiO ₂ (53.3%)
Higher LOI (1.91)	Lower LOI (1.32)
Higher levels of only Co and Cu	Higher level of trace elements (Ni, Pb, V, Zn, Mn)
Lower thermal stability (97.5) due to higher carbon content	Higher thermal stability (98.8) due to lower carbon content
More spherical particles	More irregular shaped particles

4.2.4 Low density polyethylene (LDPE)

4.2.4.1 Functional group analysis

Figure 4.11 presents the FTIR spectra of LDPE. The functional groups of LDPE are mainly alkanes (C-H). However, due to processing, other functional groups are introduced to their frameworks. A vibration mode corresponding to O-H stretch was found at 3673 cm⁻¹. This was ascribed to the atmosphere moisture absorbed on the surface of the LDPE. Prominent peaks of CH₂ stretches were observed at 2923 and 2833 cm⁻¹ wavenumber. These are typical for alkane chains that are the backbone of the LDPE structure [45]. CH₃ and CH bending appeared at 1464 and 1238 cm⁻¹ wavenumber respectively. Furthermore, C-O and O-C=O vibrational peaks were observed at 1064 and 870 cm⁻¹ wavenumber respectively [46]. These could be as a result of colorants and additives represent in the LDPE as this was not a pristine polymer but rather a recycled polymer. A sharp peak at was observed at 717 cm⁻¹, representing a CH₂ bending.

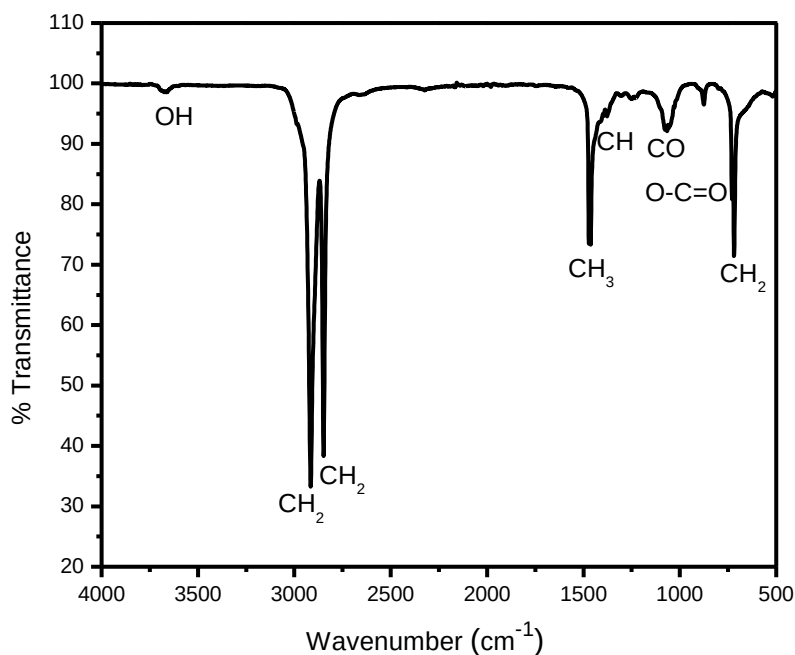


Figure 4.11: FTIR spectra of LDPE

4.2.4.2 Crystallographic analysis

In Figure 4.12, an XRD profile for LDPE is shown. It was observed that the polymer is semi-crystalline, with crystalline phases shown by the sharp peaks and the amorphous phases indicated by the broad peaks. The two characteristic peaks of polyethylene were more pronounced as it was the main component of the polymer. The peaks were observed at $2\theta = 22.06^\circ$ and $2\theta = 24.11^\circ$. For pristine LDPE, the $2\theta = 24.11^\circ$ is usually sharper and more intense than in recycled LDPE as shown. This is due to the additives in recycled LDPE which tend to influence the crystallinity of the polymer. From literature, the peaks at $2\theta = 27.61^\circ$ and $2\theta = 29.63^\circ$ have been identified as rutile (titanium dioxide) and calcite (CaCO_3) respectively. These are from the additives such as colourants used in the recycled polymer. Rutile is an oxide mineral composed of titanium dioxide and mostly used as a colouring agent in plastics, paints, paper and other applications. While, calcite is a mineral used as a white pigment to impart brightness into polymer products. It is applied to improve the resistance of the plastic against light and high temperatures and retains the colour of the plastic under various environmental conditions.

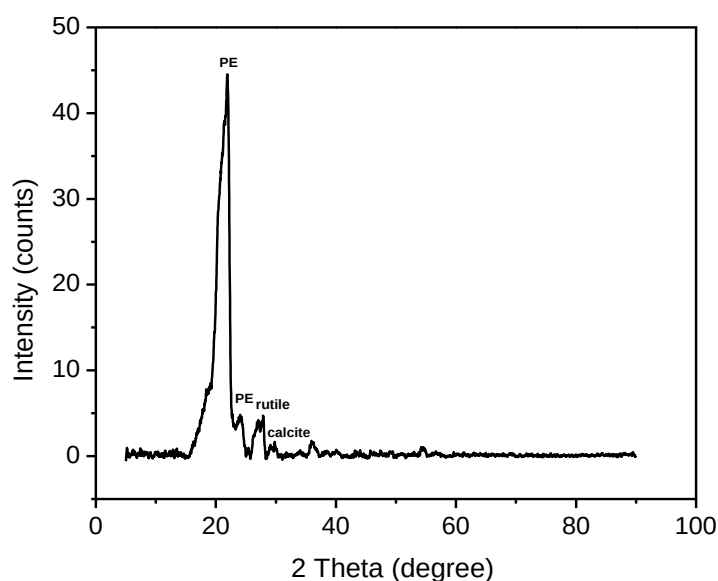


Figure 4.12: XRD profile of LDPE.

4.2.3.3 Thermal analysis

The TGA and derivative plots for LDPE are shown in Figure 4.13. A small weight loss was observed around 100 °C. This was attributed to loss of absorbed moisture which was also shown on the FTIR spectra (Figure 4.11). The major weight loss was observed at 458 °C, which was the degradation the polymer. This is consistent with other reported studies, where LDPE was recorded to decompose above 400 °C. It degrades and produce gaseous compounds with no solid mass remaining above 500 °C [47]. Understanding the thermal degradation of the polymer was important for the application in building composites. This will allow the use of sufficient flame retardant (fly ash/bottom ash and CNTs) in order to maintain the integrity of the composite.

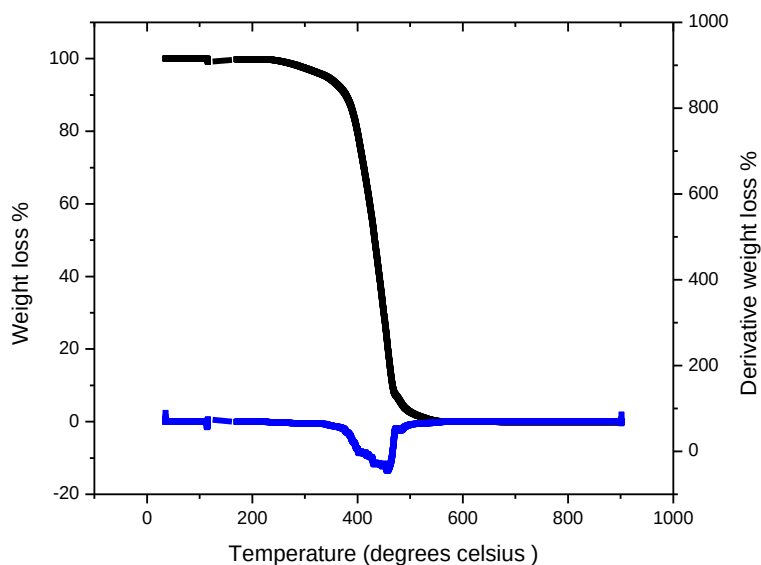


Figure 4.13: TGA plot and derivative plots of LDPE.

4.3 Conclusion

The application of waste materials in building composites is a sustainable approach towards managing pollution and ecological degradation of natural resources. Furthermore, knowing the waste material's physicochemical properties enables their application within permissible requirements and standards. This ensures consistency in the quality of the products produced by using waste materials of the same or similar properties. The characterized CFA and CBA from Lethabo Power Plant showed high thermal stability and low LOI which are properties of importance in building composites. They can act as flame retardants and stabilize polymer-based composites which are highly flammable. The two ashes had a wide particle size distribution and high levels of silica and alumina similar to that of sand, which showed their potential applicability as sand replacements in composites. However, toxic metals such as chromium were detected in the ashes, which could potentially leach and pose threats to the environment and human beings. Consequently, a polymer binder (LDPE) was added to the composite; which can potentially limit the leaching of heavy metals from the composite matrix.

4.4 References

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CHAPTER 5

APPLICATION OF CARBON NANOTUBES IN WASTE-DERIVED BRICKS

5. Introduction

The demand for sustainable building materials is growing and these materials must meet the short-term and long-term structural efficiency of buildings. Both industrialization and the growing world population has led to housing deficiencies in most developing countries [1]. The citizens migrate to urban areas for better quality of life and there they require housing. Furthermore, the fast-growing population increases the housing demand and puts a strain on the resources especially for growing economies.

Bricks are the commonly used building materials in construction activities. A brick is a masonry unit not exceeding 337.5 mm x 225 mm x 112.5 mm ($l \times b \times h$) [2]. Any unit with a dimension that exceeds any one of those specified above is termed a block [2]. Bricks are usually moulded to rectangular shapes of uniform size, dried, and at times burned (clay bricks) before application [3]. Building materials are expensive and account for 70% of the total building costs. Furthermore, bricks utilize about 65% of natural aggregates (i.e., sand and stones) [4].

There is a growing trend towards the use of inexpensive, renewable and lightweight building materials that can be as effective as the conventional ones. At the same time, policies that govern the building and construction sector are becoming more stringent, for example with the type of materials that can be used in the building industry [5]. This has led to significant research towards incorporating sustainable alternatives such as waste into building materials for use in brick manufacturing, in order to conserve the environment [6].

An example of this is the use of polymer concrete composites as an alternative to ordinary concrete composites. These composites do not contain any cement or water, while those mixed with ordinary cement, are known as polymer modified concrete bricks [7]. In polymer concrete composites, the polymer acts as a binder, while the aggregate acts as the compressive stress material [7]. A successful aggregate must be made of a good quality material and must be dry. Coal ash has been used as an aggregate in polymer concrete composites [8].

These composites are potentially 'green and sustainable' as they utilize waste/by-product materials. They are also light-weight and free of water and cement. Water disturbs polymer setting and hence the aggregates must be dried prior to application to ensure their binding capacity is not compromised [9]. Even though coal ash contains silica and is pozzolanic in nature, it only acts as an aggregate. In the composites there is no cement or water to foster the hydration reaction. Further, the spherical morphology of coal ash and their small particle sizes have been found to enhance the mechanical strength and workability in brick making [9].

Composites usually have pores, defects and voids which tends to affect their mechanical properties. Thus, microfillers such as fibers and silica can be added to improve their microstructure by producing a reinforcing framework [10]. Recently, nanofillers such as carbon nanotubes (cylindrical carbon allotropes) have become popular in reinforcing composites. This relates to their excellent mechanical properties (compressive, tensile, flexural strength) which are desirable in building composites [11]. Their superior properties result in the making of high performing composites, even when loaded in small concentrations. Generally, carbon nanotubes (CNTs) are dosed in concentrations as low of 0.01 wt.%. Even at these low dosages, composites with a strength > 20% than found for conventional bricks have been obtained [12].

In cement-based composites, CNTs speed up the hydration reaction by acting as nucleation sites and increase adhesion with cementitious hydration products [13]. In polymer concrete composites, CNTs reinforce the brick by filling voids, and facilitate the bridging effect as well as load transfer which hinders microcrack propagation [14]. The bridging effect by CNTs is when they are adjacent to the crack, shield the crack front from carrying the entire load applied. Thus, acting as a crack arrestor due to which the crack resistance and fracture toughness increases [14].

However, the challenge with using CNTs in composites is their tendency to agglomerate. This is due to their large surface areas which induces strong attractive forces (Van der Waals) between CNTs [15]. At low dosages, high CNT dispersion is possible, which is required for maximum mechanical performance [16]. Different approaches such as the use of surfactants and ultrasonication have been adopted to ensure a homogenous dispersion of CNTs within the composite. Covalent bonding is involved in chemical functionalization, which is the most

often utilised technique. Strong acids, such as sulfuric and nitric acids, are typically used in chemical functionalization processes to introduce oxygenated functional groups. These functional groups enable the CNTs to disperse in solvents and other matrixes. Further, the functionalized CNTs have improved interfacial interactions within the composite which enhances their reinforcement ability [16].

CNTs have been used to reinforce partially replaced coal ash-cement composites or polymeric composites. However, to the best of our knowledge they have never been used to reinforce all waste (coal ash and waste LDPE plastic) bricks completely free of cement or clay. Conventional building bricks are usually made of clay or cement and composites of these materials have been tested for their strength and ability to be load bearing. Thus, the application of CNTs in bricks without strength developing aggregate materials (cement/clay) will be crucial as they will be the material responsible for reinforcement and load transfer. The coal ash will only act as an aggregate due to the absence of water. It cannot impart its pozzolanic properties which are known to facilitate the hydration reaction and strength development of geopolymer composites. Usually, coal ash and other waste materials such as waste plastics and glass are partially added (maximum of 40%) to clay or concrete bricks but never used as the only aggregate materials as in this study.

The conventional method for making bricks involves wet mixing (with water) of aggregates and casting them in the mould and lastly -in the case of clay bricks- firing the final brick product [3]. However, in this study the process involved melting LDPE and mixing it with the aggregates, then casting into moulds and air drying the final brick product. Functionalized multiwalled carbon nanotubes (*f*-MWCNTs) were made in this study and used to reinforce the LDPE-coal ash bricks. Their effect on the mechanical properties (compressive and tensile strength), water absorption, density and microstructure were investigated. The brick samples were incorporated with different dosages of *f*-MWCNTs, (0.00 wt.%, 0.01 wt.%, 0.05 wt.%, and 0.1 wt.%).

5.1 Methodology

The outline of the process used to develop the bricks is shown in Figure 5.1 and the mix design is presented in Table 5.1. Weighed amounts of shredded low-density polyethylene (LDPE)

plastic waste was melted for 30 min and the dried coal ash (either coal fly ash (CFA) or coal bottom ash (CBA)) was added to the melted LPDE. The mix was blended in a reactor for 20 min or until homogenous. The mix was then cast in a mould (220 x 105 x 70 mm) and compacted at 40 MPa to make control bricks (i.e., with no CNT added). In other experiments, CNTs (0.01, 0.05 and 0.1 wt.%) were added to the LDPE-coal ash mix to make CNT reinforced bricks. The CNTs added were those synthesized and functionalized as detailed in Chapter 4. The bricks were left for 30 min to air dry and were kept for testing.

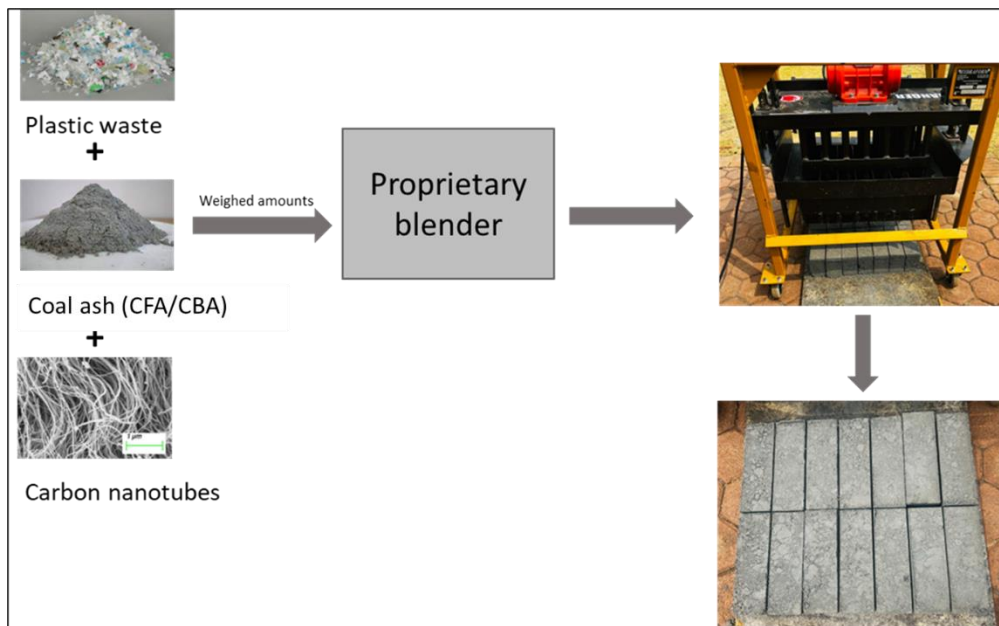


Figure 5.1: Schematic of the method used to make the bricks

Table 5.1: Mix design of the developed bricks

Sample ID	CFA	CBA	LDPE	CNTs
	wt.%	wt.%	wt.%	wt.%
1.	80	0	20	0
2.	85	0	15	0
3.	90	0	10	0
4.	0	80	20	0
5.	0	85	15	0
6.	0	90	10	0
7.	85	0	15	0.1
8.	85	0	15	0.5
9.	85	0	15	1

5.2 Tests performed on the bricks

5.2.1 Workability

The bricks were tested for workability during mixing to determine the optimum working ratio. This was to ensure homogeneity of the composite and sufficient binding of the polymer with the dry ingredients. The ratio of the aggregate to binder was varied at 80:20, 85:15 and 90:10 respectively.

5.2.2 Compressive strength

The bricks were tested for compressive strength using an Amsler compression testing machine according to ASTM C67. Three brick samples of different compositions were tested. The samples were tested in the direction that bricks would be typically laid (which is the side with the higher surface area). A loading rate between 1 ± 0.5 kN/s was applied until failure occurred. The load at failure was then recorded and used to compute the compressive strength using the formula below [16]:

$$CS = \frac{F}{A} \dots\dots\dots [5.1]$$

Where CS is the compressive strength (in MPa), F is the force/load at failure (in N) and A is the cross-sectional surface area of the specimen in (in mm²).

5.2.3 Split tensile strength

The bricks were tested for split tensile strength using a compression testing machine (Figure 5.2) according to ASTM C1006–07. A 2.16 kg steel block with a length of 224.7 mm and diameter of 10 mm was placed in the middle of the brick and a loading rate between 1 ± 0.5 kN/s was applied parallel to the edges along the length of the brick, until failure occurred.



Figure 5.2: Split tensile strength testing setup

5.2.4 Density

The density of the bricks was determined by measuring the mass and dimensions of each specimen and recorded in kg/m³ and the tests were done in triplicate.

5.2.5 Water absorption

The water absorption capacity and deformations due to water absorption were conducted simultaneously on test bricks according to ASTM 607. Prior to testing, the bricks were left in

an oven (maintained at a temperature of 50 °C for 24 hours) and the mass recorded daily until a constant mass was reached. The initial length of the bricks was also measured.

The brick samples were then submerged in a water tank at $22 \pm 1^\circ\text{C}$, for 24 ± 2 hours. Following this period of submergence, the samples were removed from the water tank, and new mass and length readings were immediately recorded. The samples were then placed back in the water tank. Subsequent readings were then taken every 24 ± 2 hours until the mass and strain (length) readings remained constant.

5.3 Results and discussion

5.3.1 The effect of mixing ratios on the workability

The workability of composite describes the compatibility of the mix components, i.e., their mobility and their stability. It gives information on the consistency and homogeneity of the mixture and thus, the quality of the final composite [17]. Table 5.2 records the workability data obtained on the brick samples at different mixing ratios. Three mixes of the same composition were prepared to make the bricks. These mixes were chosen because bricks with the lowest amount of LDPE while sufficiently bond were desired to reduce their risk of flammability. Figure 5.3 represents bricks developed with coal fly ash, it was noted that the 80:20 (coal fly ash: LDPE) ratio resulted in a soft mix that accounted for bricks that were too soft and were slightly deformed after compaction (Figure 5.3a). The 90:10 ratio resulted in a hard mix that had insufficient polymer to bind the coal ash aggregate. The bricks were fragile with the surface grains easily breaking down and exposing new sharp edges (high friability) of the brick (Figure 5.3c). The optimum ratio was found to be 85:15 and this was used for both CFA and CBA for comparability in separate experiments. This ratio resulted in good bricks that were well compacted (Figure 5.3b). The optimum ratio was used in all further studies where the effect of CNT dosage on the properties of the bricks was investigated.

Table 5.2: Mixing ratios of raw materials

Sample ID	Coal ash (CFA/CBA)	LDPE	Results
a)	80	20	Too wet (deformed bricks)
b)	85	15	Mixes well
c)	90	10	Does not mix well



Figure 5.3: Brick samples using different coal fly ash : LPDE ratios. a) 80:20, b) 85:15 and c) 90:10.

5.3.2 Compressive strength

5.3.2.1 Compressive strength development

Compressive strength tests were performed on both the CFA/CBA-LDPE bricks at 85:15 ratio respectively. This test determines the amount of load a brick can handle and consequently, the type of application the bricks can be used within the building and construction fields. The compressive strength of conventional concrete bricks improves with time due to the

hydration process that gradually takes place in a brick and the tests are performed after 28 days [18]. To study the effect of compressive strength development of the coal ash-LDPE bricks relative to the conventional bricks they were tested over 28 days of casting. The effect of time on the compressive strength of the CFA and CBA bricks was studied at day 3, 7, 14 and 28 after casting. Figure 5.4 presents the strength development data for the coal ash bricks over the 28 days. It was noted that for both the CFA and CBA bricks, the compressive strength improved with time. The maximum compressive strength at day 28 was 12.1 and 10.9 MPa for CFA and CBA bricks respectively. However, unlike the conventional bricks, the strength development of the coal ash-polymer bricks showed no significant improvement after 14 days. These findings were similar to those of Sokolowska, where it was observed that for polymer composites (vinyl ester-fly ash), the strength development was 60% within the first day of casting and reached up to 80% within 3 days [19]. This was due to the dynamics of setting and curing of the polymer binder. The process rapidly goes through a gelation phase and then polymerization to create a cross-linked framework in the polymer matrix [20]. Thus, polymer composites develop their properties as a function of time.

The results obtained showed CFA composites to have a slightly higher compressive strength compared to those of CBA. This could be attributed to the smaller particle sizes of CFA as compared to CBA (see section 4.2.1.3 and 4.2.2.3) which might have affected the porosity of the bricks and thus their compressive strength. CFA particles are generally finer while those of CBA are heavier [21]. Furthermore, the moisture content of CBA was higher than that of CFA, as confirmed by TGA measurements (see section 4.2.1.5 and 4.2.3.3). Water disturbs or prevents the setting of polymers which can affect their ultimate compressive strength [22]. From the above data, CFA bricks cured for 14 days were used in all later studies.

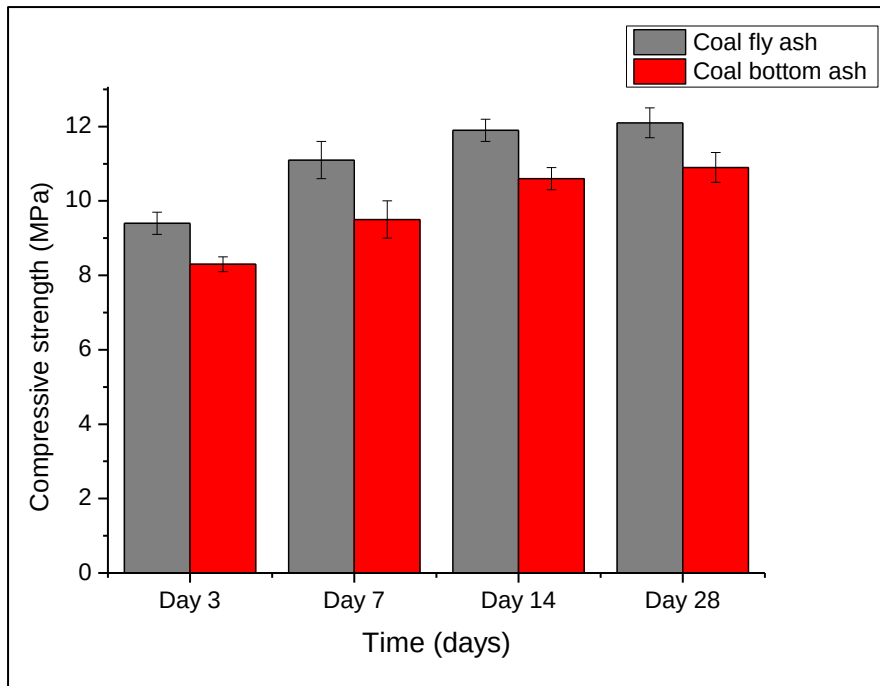


Figure 5.4: Compressive strength development of CFA and CBA bricks with time

5.3.2.2 Effect of CNT dosage on the compressive strength

Figure 5.5 shows the compressive strength of CFA bricks at different CNT dosages after 14 days of curing. The compressive strength of the bricks increased with an increase in CNT loading. The strength improved from 11.9 to 17.2, 22.4 and 25.4 MPa for the control, 0.01, 0.05 and 0.1 wt.% CNT loadings respectively. These results showed that low CNT dosages can significantly improve the compressive strength of composites. However, the results obtained in this study for the 0.1 wt.% CNT dosage showed substantial variation which resulted in a large error margin of ± 6 MPa. This was attributed to agglomeration of the CNTs at the higher loading, resulting in the formation of an inhomogeneous matrix. Agglomeration within a composite matrix can result in weaker spots that are prone to microcracks. The small CNTs are presumed to fill the voids within the composites and also created a bridging effect that minimize microcracks within the matrix when stress is applied. Furthermore, their long length enabled effective load transfer, thus reinforcing the composite [23]. Studies have been reported by other researchers on the addition of low CNTs dosage (0.01-0.2 wt.%) to related materials [24–28]. It was recorded that at low dosages, there was better dispersion which enabled the CNTs to be effective in reinforcement. Their surface area was not compromised

and for the functionalized CNTs, the treated surfaces were better exposed for interaction within the composite. Similar results have been reported where cement mortars dosed with CNTs (0.01, 0.015 and 0.02 wt.%) resulted in an increase in the compressive strength of the mortar. This was attributed to densified cement-CNT clusters that limited crack initiation, propagation and distribution [29].

The recommended ASTM C67-03 and SANS227:2007 compressive strength requirements for building bricks are: 4.0 MPa for on-site building, 5.0 MPa for off-site building, and 10 MPa for multi-story buildings [30]. All the new bricks surpassed the 10 MPa requirement (Figure 5.5). Further, at their load of failure, the bricks were not crushed but did show some minor cracks (Figure 5.6). However, beyond their load of failure the bricks (0.05 wt.% CNTs) shown in Figure 5.7 ruptured. This phenomenon of crack distribution upon applied load was not observed upon the addition of the CNTs. Minor cracks at different areas were shown, suggesting that the CNTs prohibited the continuation of cracks after they were initiated. It was observed that as the CNT dosage increased, the porosity of the bricks was reduced (Figure 5.6), due to the CNTs which further increased their compressive strength. The cracking mode of the bricks was classified as ductile and this is usually observed for polymer composites [31]. This type of crack will not continue unless the applied stress is increased and it generally ceases continuation when the load is removed. Polymer composites usually undergo significant plastic deformation before rupture, which was observed with the developed bricks [31].

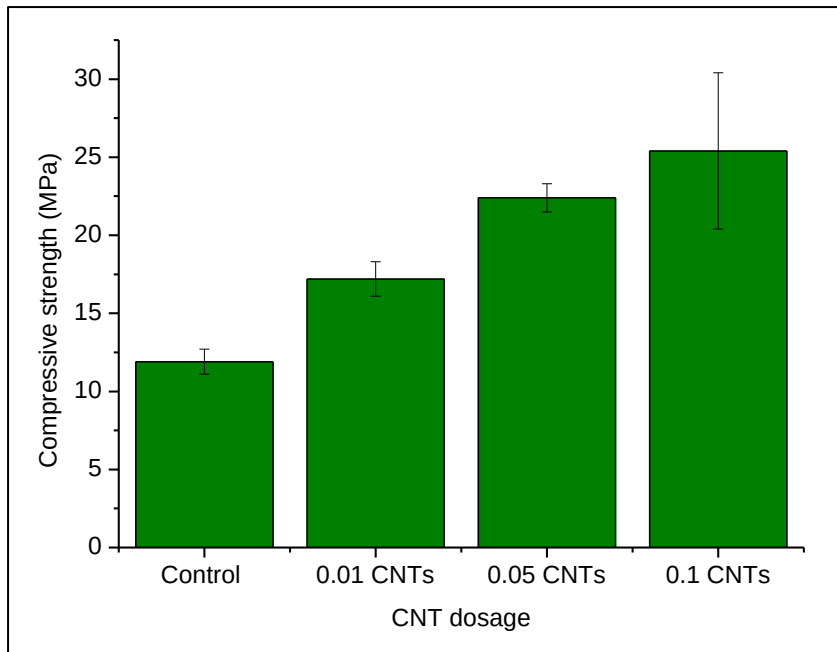


Figure 5.5: Compressive strength of coal fly ash bricks with different CNT dosages

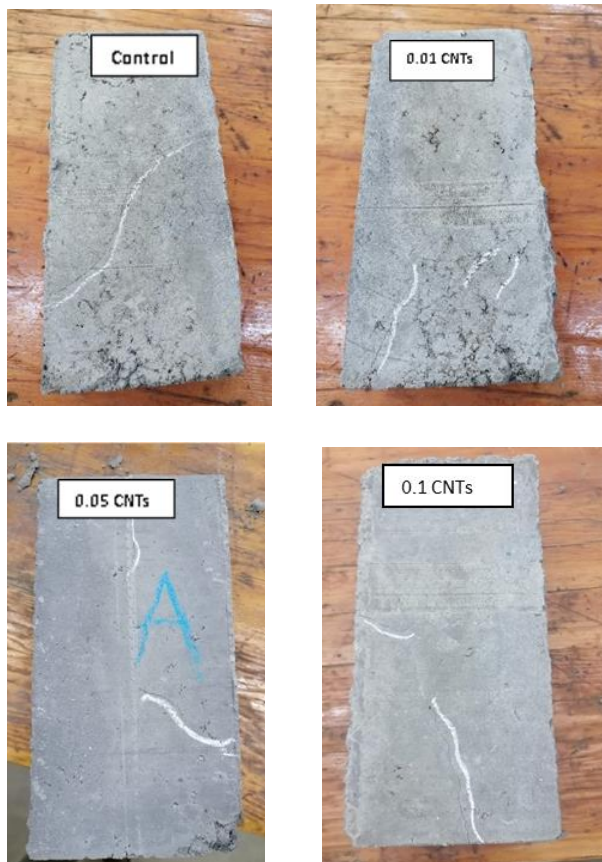


Figure 5.6: Bricks after compressive stress was applied



Figure 5.7: Stress beyond load of failure applied on the 0.05 wt.% CNT brick

5.3.3 Split tensile strength

Figure 5.8 shows data for measurement of the tensile strength of the CFA bricks with different CNT dosages, after 14 days of curing. The split tensile strength was found to be 3.2, 5.4, 8.7 and 9.8 MPa for the control, 0.01, 0.05, and 0.1 wt.% CNT samples respectively. Similar to the compressive strength, the tensile strength increased with an increase in CNT dosage. This was attributed to improvements in the microstructure upon the addition of CNTs, making the bricks denser and more compact. It was observed at 0.05 and 0.1 wt.% CNT dosages that the crack, upon tensile stress, was deflected and did not continue all the way to the end of the brick (Figure 5.9).

The width and length cracks were measured and recorded in Table 5.2. The control and 0.01 CNT bricks cracked until the end and the crack length were similar to their length of 224 and 223 mm respectively. The 0.05 wt% had a length crack of 198 mm and 186 mm for the 0.01 wt.% (including the deflected crack). The recorded width crack was 4 mm, and 1.5 mm, 0.4 mm and 0.15 mm for the 0.0, 0.01, 0.05 and 0.1 wt.% CNT respectively. It was observed that the width and length cracks were reduced upon increased CNT dosage. The recorded width

This showed the bridging effect phenomenon due to the presence of the CNTs, that prohibited the crack propagation. CNTs are similar to carbon fibers in their shape and size, Both, when added to composites, work to remove microcracks and to bridge the cracks. These effects increase the bonding between two sides of a crack and hence increases the split tensile strength [4]. According to the ASTM C16, the split tensile strength of building bricks should be 1.2 MPa [32]. All the bricks in this study satisfy the requirement.

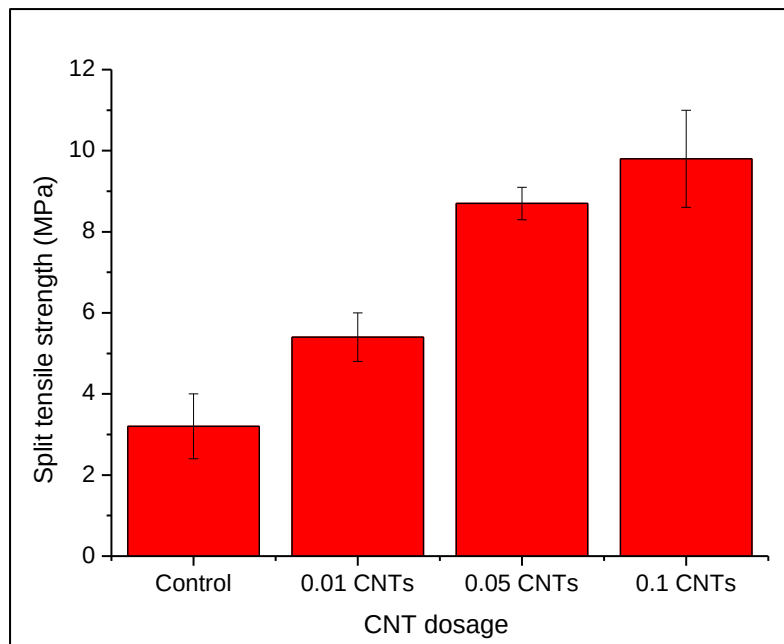


Figure 5.8: Split tensile strength of coal fly ash bricks with different CNT dosages

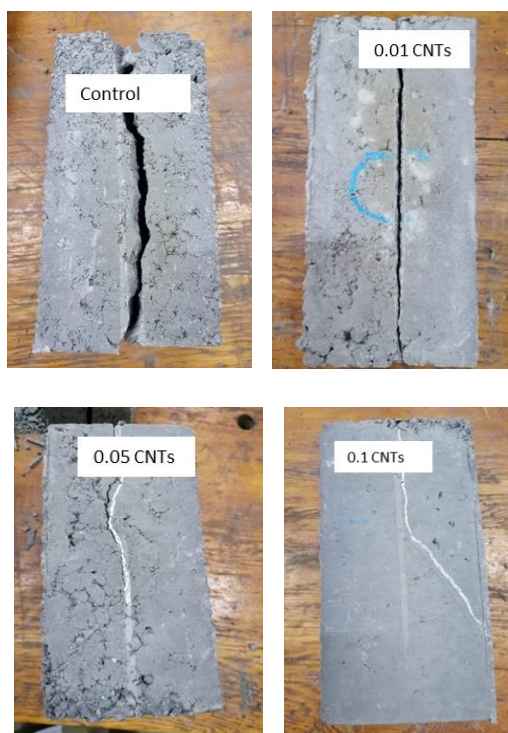


Figure 5.9: Bricks after the split tensile stress test

Table 5.3: Crack measurements after split tensile stress

Material	Crack width (mm)	Crack length (mm)
Control	4	224
0.01 CNTs	1.5	223
0.05 CNTs	0.4	198
0.1 CNTs	0.15	186 (including the deflected)

5.3.4 Density

Table 5.3 lists the dimensions, mass and density of the bricks made in this study. The average dimensions of the bricks were 224 mm x 102 mm x 71 mm. These were comparable with the 222 mm x 106 mm x 73 mm dimensions of conventional bricks according to the South African Bureau of Standards (SABS) [33]. The variation in the dimensions of bricks should be ± 2 mm length, ± 1.5 mm breadth, ± 1.5 mm depth for the bricks to be considered good quality [33]. A great variation in the dimensions could be as a result of variations in raw materials properties, manufacturing processes and the moulds [34]. The bricks in this study had a dimension

variation of ± 2 mm length, ± 1 mm breadth and ± 1 mm depth; within the permissible range. The average mass of the bricks was 2.5 kg which was lower than the conventional bricks that have a mass of between 3.0 kg and 3.5 kg [35]. This also accounted for an average density of 1577 kg/m^3 . The density of the bricks increased with an increase in CNT dosage (Table 5.3). This was attributed to the reduced porosity of the bricks as a result of the CNTs acting as a filler to occupy the voids within the composite. However, the density data were still less than the typical concrete density of 2400 kg/m^3 ; but fell within the typical clay brick density range of 1225 kg/m^3 to 2190 kg/m^3 [36]. The low mass and density were due to the presence of the waste materials (coal ash and plastic) which are lighter than the conventional building aggregate materials such as cement, stones. It was also observed in another study that the introduction of waste materials such as plastics and crushed glass into concrete bricks reduced their density due to the low unit weight of the additive [37]. Density plays an important role in the construction sector and recently the generation of lighter building materials has become desirable. This is due to the easier transportation of lighter bricks and that lighter bricks are easier to handle during construction. This has a direct impact on construction time and thus, the overall costs [38].

Table 5.4: Dimensions, mass and density of the coal fly ash bricks

Sample ID.	Average length (nearest mm)	Average width (nearest mm)	Average depth (nearest mm)	Mass (kg)	Density (kg/m^3)
Pristine	224	102	71	2.510	1547
0.01	223	101	71	2.525	1579
0.05	225	102	71	2.560	1587
0.1	224	101	70	2.585	1596

5.3.5 Microstructure analysis

Figure 5.10 shows the SEM images of CFA bricks reinforced with different CNT dosages. Figure 10 a) represents the control composite (0 wt.% CNTs) and it was observed that there were several unoccupied spaces within the composite, meaning it was not fully compact. Thus, accounted for the lower density and higher water absorption compared to the other composites. Furthermore, the control composite had the lowest compressive and tensile strength because the voids assisted in microcrack propagation under an applied load.

When 0.01 wt.% CNTs was dosed to the composite (Figure 5.10b) it was observed that the CNTs reinforced the composite through the bridging effect. The CNTs bridged the gaps between the aggregates and thus, aided load transfer within the matrix when stress was applied. In Figure 5.10c), a CFA composite with 0.05 wt.% CNT is shown. The CNTs were seen to be well dispersed within the composite, which is desirable for reinforcement fillers. This was due to their functionalization through acid treatment which is known to improve dispersion [39]. At this dosage, the CNTs were able to fill the voids within the composite matrix which densified the structure as well as aided in the bridging effect.

The CNT networks are expected to provide stronger resistance to deformation [40]. Thus, a composite with 0.05 wt.% CNT dosage showed high compressive and tensile strength. Upon an applied load, the CNTs within the composites deflected the cracks and prohibited their continuation (Figure 5.8). Similarly, Chaturvedi et al., reported that hydroxyl functionalized CNTs were well dispersed in fly ash composites and no cracks or voids were then observed indicating strong interfacial bonding [41]. Figure 10 d) shows CFA composites with 0.1 wt.% CNT dosage. It was observed that the increase in CNT dosage to 0.1 wt.% resulted in CNT agglomeration. The CNTs were not as well dispersed and were concentrated in specific regions within the matrix. This was due to the strong Van der Waals forces that exists between the CNTs [27]. At high dosages, the CNTs tend to be attracted to each other and agglomerate [42]. The bundled-up CNTs led to increased micro-voids which caused inconsistencies in the compressive and tensile strength results. Tests were done in triplicates, and data showed that the inhomogeneity in the composite mix resulted in a large margin of measurement error and poor repeatability.

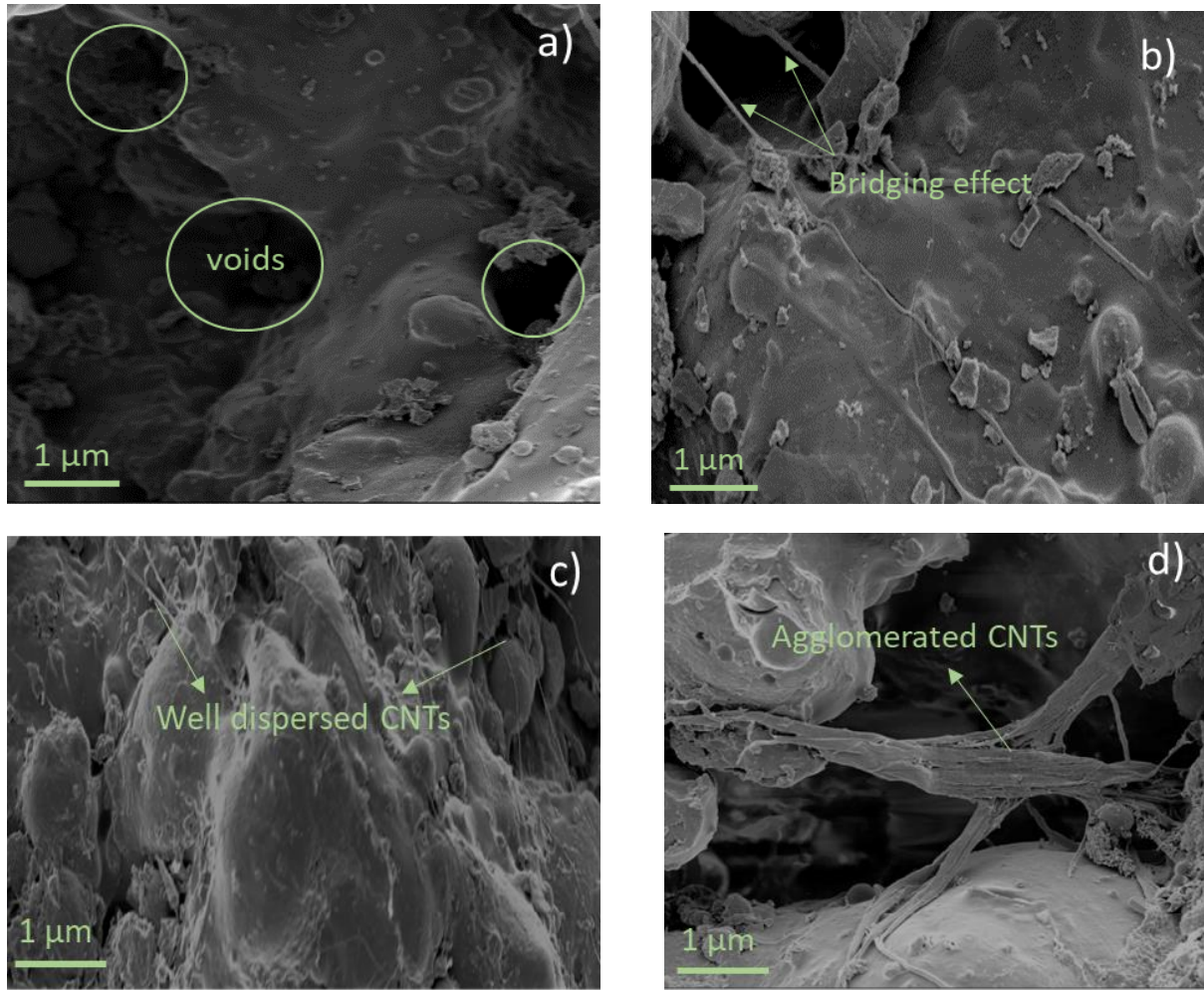


Figure 5. 10: SEM images of CFA bricks reinforced with different CNT dosages a) control, b) 0.01 wt.% and 0.05 wt.% c) 0.1 wt.%

5.3.6 Mechanism of interaction and reinforcement

The CNTs need to be well-dispersed in the composite for efficient reinforcement and this was achieved as shown in Figure 5.10 c) through acid treatment with nitric acid. Acid treatment allows the surfaces of the CNTs to be functionalized with polar oxygen-containing groups (-COOH , C-O , and -OH). Figure 5.11 represents the FTIR spectrum of the brick composite with 0.05 wt.% functionalized CNTs ($f\text{-CNTs}$). A minor carbonyl group of C=O was observed at 1462 cm^{-1} and at 1698 cm^{-1} the C-O peak was more prominent than in the control. This indicating the incorporation of the CNT's functional groups in the matrix of the composite. The other peaks at 2055 , 2854 and 2924 cm^{-1} were assigned to CH_2 for CNTs as well as for LPDE whose

backbone is alkyl groups. The other peaks at 1066, 552 and 446 cm^{-1} were the distinctive O-T (T=Al/Si) peaks of coal ash.

It has been suggested that by encouraging electron exchange between carbon atoms and a metal matrix, oxygen functional groups may enhance interfacial binding (Figure 5.12) [43]. Coal ash contains several metals (i.e., Al, Si, Fe) (see section 4.2.1.1 and 4.2.2.2) and the functional groups may enhance bonding between the metal matrix and the CNTs. Further, the functional groups in CNTs can improve interfacial interactions with the carbon atoms from the LDPE polymer chains. In composites reinforced with nano-fillers such as CNTs, interfacial shear stress enables the stress to be shifted from the matrix to the reinforcement. Effective load transfer is dependent on the strength, chemical stability, length, aspect ratio, and quality of the interface bonding, concentration, and uniform dispersion of the reinforcement filler material [44]. The CNTs used were highly crystalline ($I_D/I_G=0.44$) which relates to high strength CNTs [45], had a length of 214 μm and a high aspect ratio of 2578 (see Chapter 3). As a result, the load transfer strengthening mechanism was able to absorb a significant amount of fracture energy, which greatly reduced the propagation of cracks and improved load bearing ability of the composite.

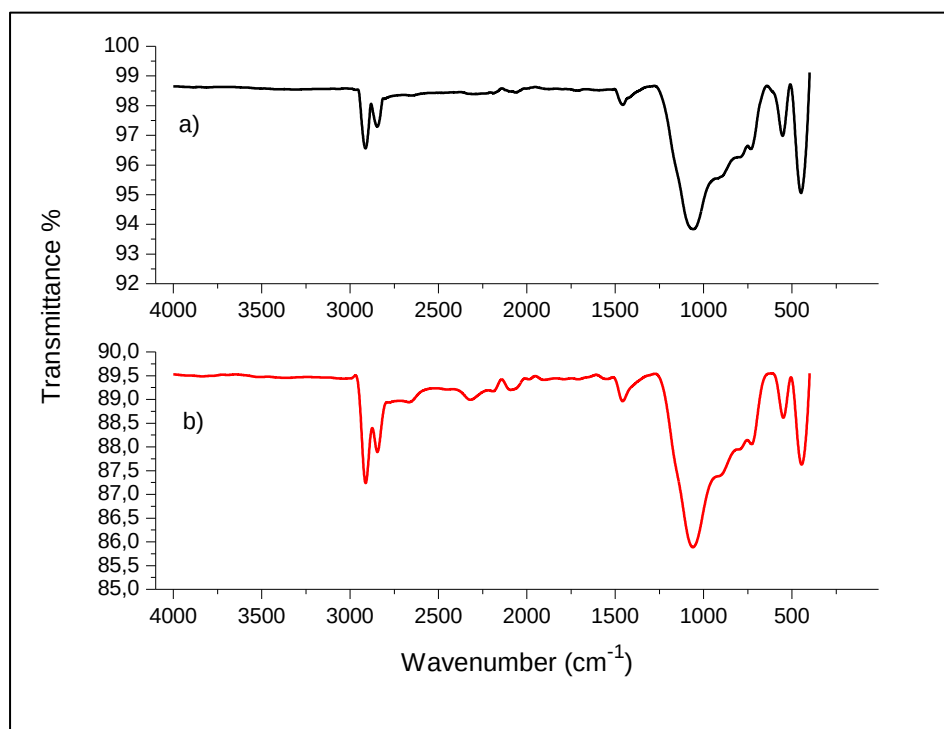


Figure 5.11: FTIR spectra of the brick a) 0.0 wt.% (control) and b) 0.05 wt.% CNT dosage

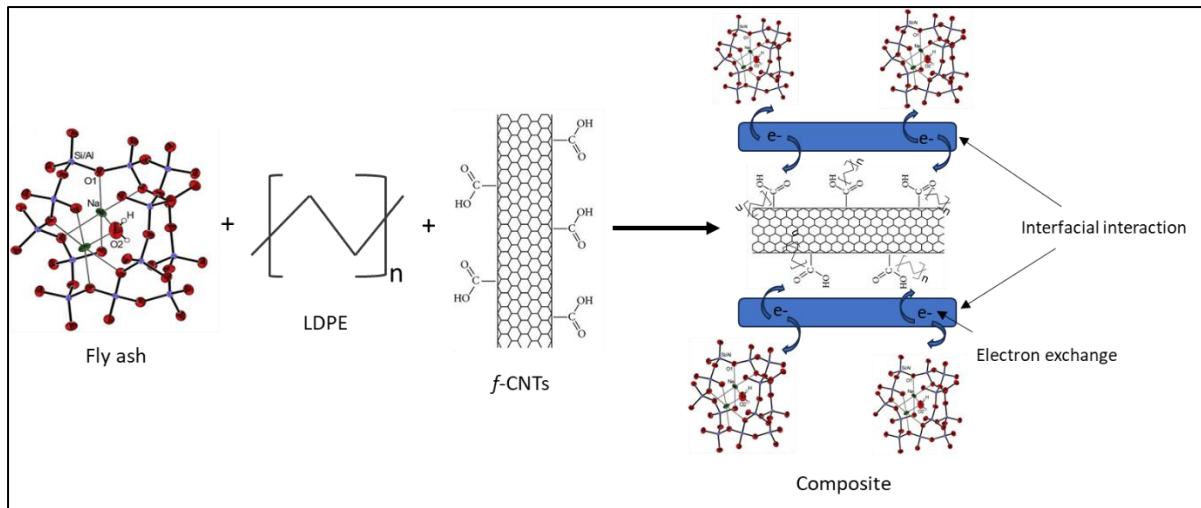


Figure 5.12: Schematic representation of the possible mechanism of interactions between the different materials applied in the preparation of bricks

5.3.7 Water absorption and deformation

Absorption experiments were performed to measure the amount of water taken up to fill pores in a brick. This is done by displacing the air with the water. Tests were run to determine the degree of compactness of the bricks and consequently the porosity of the bricks. The tests give information about the quality, durability and weathering properties of the bricks [46]. It has been reported that bricks with a water absorption below 7% are less prone to damages from freezing and thawing [47]. Water absorption tests were performed on the bricks and the mass variation of the bricks during water absorption was reported as a percentage of the brick's original mass before being submerged in water.

Figure 5.13 a) illustrates the mass variation of the bricks during water absorption over time. The water absorption rate for the bricks was high in the initial stages (day 1) but slowed down. The first absorption was rapid absorption due to capillary pores and macro void. Micropores known as capillary pores have a diameter of up to 1 μm , whereas macro voids have a diameter of more than 10 μm . The second step, known as steady absorption, denotes the entry of water at the capillary pore's top and its subsequent transfer into gel pores. These pores are smaller, measuring about 2 nm [48]. Diffusion limitation applies to this water transport into gel. Additionally, it was noted that reference bricks exhibited greater water absorbance than CNT bricks during the exposed duration.

The water uptake of CNT bricks started to stabilize at day 8. While, the control bricks experienced continued water absorption and began to stabilize at day 11. After 14 days, the amount of water absorbed by the bricks was 3.5%, 3%, 2.7% and 2.4% for the control (0.0), 0.01, 0.05 and 0.1 wt.% CNTs dosage respectively. This value was lower than both clay and concrete bricks, which have water absorption values of 4.5 to 21% and 7 to 10% respectively. Bricks with water absorption of less than 3% are called vitrified (low porosity) bricks [46]. The developed bricks all showed low water absorption due to the presence of the LDPE polymer. Plastics are usually hydrophobic and do not absorb or transfer any water, and this property was also reflected in the analysis of the bricks containing the LDPE. The water absorption also decreased with an increase in the CNT dosage. CNTs act as a nanofiller and occupy voids within a composite which reduces their porosity. Li et al., reported similar findings where a high CNT dosage gave less water absorption of a fly ash [48].

The deformation due to water absorption was calculated as a ratio of the change in length over the initial length and is expressed in units called microstrains ($\mu\epsilon$) [36]. Figure 5.13 b) illustrates the strain variation during water absorption. The deformation was reduced when the CNT loading was increased. This was attributed to the improvement in the microstructure of the bricks which reduced their deformation due to water absorption. There was significant deformation (change in length) of the bricks for the first 8 days. After this they started to stabilize and thereafter a similar trend was observed for water absorption. The trendlines suggests the maximum strain value was approximately 260 microstrains for the control (0 wt.% CNTs) bricks. A value of 200 microstrains is typically found for clay bricks, while the values range between 200 and 400 microstrains for concrete [36]. This showed that all the bricks were within the acceptable strain values.

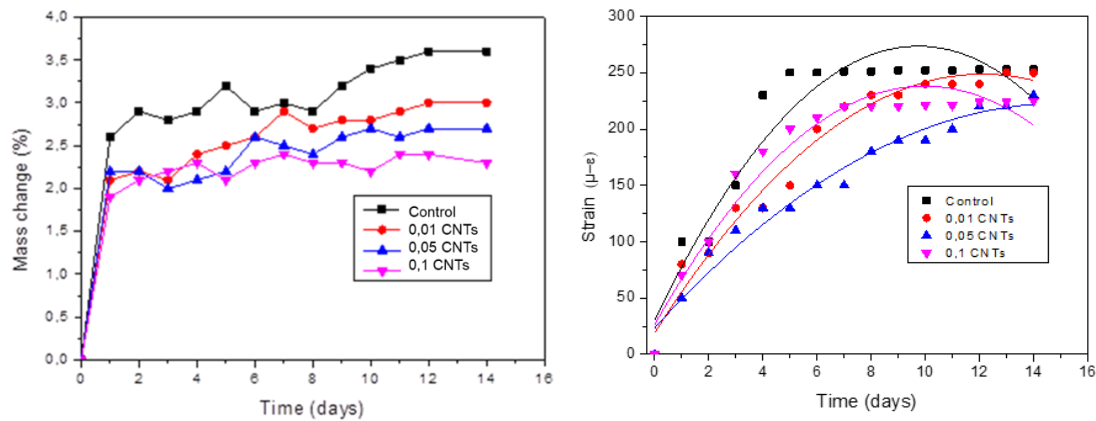


Figure 5.13: a) mass variation during water absorption and b) deformation due to water absorption of bricks

5.3.8 Current study and comparative literature data

Table 5.4 shows comparative data where CNTs were used to reinforce construction composites. It must be noted that the reported data is for cement/ geopolymers mortars not for building bricks as is in this study. There was no literature found where CNTs were used in building bricks. However, a similar trend was observed where the inclusion of CNTs at low dosages improved the compressive strength. This was attributed to improvements in the microstructure which resulted in densified and compacted composites. Even though most of these studies did not report on the density but Chiapanchi et al., similar to this study, observed an increase in density with an increase in CNT dosage [24]. Higher CNT dosages of up to 5 wt. % were used [49] and a reduction in compressive strength beyond 1 wt. % was recorded. This was as a result of agglomeration at higher dosages. Some of these studies used unfunctionalized CNTs and reported poor dispersion as well as insignificant strength development. Further, some mortars were cured beyond 28 days (up to 60 and 90 days) and more strength development was observed. It was not the case for this study, as the LDPE (used as a binder) has a higher settling rate than cement and as early as day 14, significant strength development was attained.

Table 5.5: Studies on CNT-reinforced composites

Mix ingredients	Application	CNT dosage (wt.%)	Dispersion method	Max. days aged	Compressive strength (MPa)	Density (kg/m ³)	Ref
Cement, water, coarse & fine aggregate, superplasticizer	Cement mortar	0 0.01 0.02 0.3	-	28	29 31 33 35	-	[50]
CFA, cement, NaOH, Na ₂ O water	Geopolymer mortar	0 1 2 3 4 5	-	28	34 37 25 20 17	-	[49]
Cement, water, superplasticizer	Cement mortar	0 0.125 0.25 0.5	Acid treatment & sonication	28	62 65 71 62	-	[51]
CFA, cement, water	Geopolymer mortar	0 0.5 1	-	60	50 54 55	2190 2290 2290	[24]
CFA, cement, water	Geopolymer mortar	0 0.05 0.1 0.15	Acid treatment & SDS dispersant	28	45 48 55 46	-	[48]
Cement, clay, water, superplasticizer	Cement mortar	0 0.02 0.05 0.1	-	90	79 82 102 104	-	[23]
CFA, LDPE	Bricks	0 0.01 0.05 0.5	Acid treatment	28	12 17 22 25	1547 1579 1587 1596	Current work

5.4 Conclusion

The effect of MWCNTs dosage (0.01, 0.05 and 0.1 wt.%) on the properties of the waste (coal ash and LDPE plastic) derived bricks was studied. The properties measured were the mechanical and tensile strength, density, microstructure, water absorption and deformation. The MWCNTs were functionalized through acid treatment for better dispersion within the composite. The mechanical strength development upon curing time (28 days) was studied and it was observed that CFA bricks had a higher strength compared to the CBA bricks. CFA

bricks were thus used to study the effect of MWCNTs on the bricks. The optimum curing time was found to be 14 days and beyond that no significant strength development was observed. This showed that the bricks, due the presence of LDPE polymer - which has a faster setting rate- had a shorter curing time compared to the conventional bricks. Consequently, all the tests were performed on 14 days cured bricks. The mechanical strength (compressive and split tensile) improved when the CNT dosage was above 0-0.1 wt.%. The compressive and split tensile strengths were above the required standard of 4 MPa and 1.2 MPa respectively for all the bricks. It was observed that at higher CNT dosage (0.05 and 0.1 wt.%) the microcrack propagation was inhibited by crack deflection. This was attributed to improvements with the microstructure of the composites which showed CNTs fill the voids as well as introduce a bridging effect which reinforced the bricks. The composites were densified at higher CNT dosages. However, at 0.1 wt.% mechanical strength measurements gave variable results. This was due to the CNT agglomeration at the higher dosages which resulted in inhomogeneous composites mixes. The developed bricks had a low water absorption due to the presence of the LDPE polymer which is hydrophobic. The water absorption was further reduced when the CNT loading was increased, as a result of the formation of more densified bricks which indicated reduced porosity. Lastly, the deformation due to water absorption (reported as strain) reduced with an increase in CNT dosage. However, all the bricks had strain values comparable to the conventional bricks (200 and 200-400 microstrain for clay and concrete bricks respectively). The CNT/waste-derived bricks show great potential in application as sustainable alternatives to building bricks.

5.5 References

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CHAPTER 6

DURABILITY OF WASTE-DERIVED CARBON NANOTUBE REINFORCED BRICKS

6. Introduction

The durability of building bricks is an important measure of their sustainability and applicability. The term refers to the amount of time a brick can maintain its integrity when used in construction [1]. The durability of the bricks can be affected by many factors such as their quality and their environmental exposure. Pollutants and contaminants that can deteriorate bricks in the environment include carbon dioxide, nitrate, nitrite, ammonia, salts and particulate matter [2]. Chemicals such as acids and sulphates may also attack a building made of bricks and corrode the building structure. In ground water, sources of sulphuric acid can arise due to the oxidation of sulphide minerals such as marcasite and pyrites [3]. Chemical attack tests are thus undertaken to ascertain the durability of bricks in acidic (and basic) media.

Water may enter the bricks from the ground, by condensation, by rain entry through the cracks or by surface absorption. Cracks are the principal means by which water enters the bricks and its effect can be significant. The water that enters the bricks may contain chemicals such as salts; salts may also be present after the water has evaporated from the bricks [4]. When water evaporates, the salt deposited on the surface of the brick is called efflorescence. Efflorescence is more of an aesthetic problem rather than a durability one. However, it can be an indication of cryptoflorescence, which is the evaporation of water with salt within the brick, which can be destructive [5].

The excessive costs related to repairing and rehabilitating infrastructure is detrimental for a country's infrastructure and economy, especially for developing economies like South Africa. It affects the construction of facilities such as hospitals, schools and homes. Thus, it is crucial to establish methods that can ensure that the structures built are durable.

Three durability index (DI) tests for concrete materials have been developed by South African researchers [6]. These have been in use for more than 20 years for the determination of concrete reproducibility, and repeatability [6]. The DI tests include oxygen permeability (gas

diffusion), chloride conductivity (ion diffusion) and water sorptivity [7]. Each test evaluates a different characteristic of fluids or ions as they move through the concrete's top layer. The concrete's ability to remain durable is determined by how exposed the concrete is to various transport mechanisms, which control how quickly the concrete can deteriorate [8]. The tests have shown to be sensitive to characteristics of concrete construction that are relevant to durability. These factors include the materials, their compaction and curing. For example, the chloride conductivity index (CCI) is used to estimate chloride infiltration, while the oxygen permeability index (OPI) is a prediction technique for evaluating carbonation depths in structures [9].

The DI tests were used to determine the durability of the bricks made in this study. They were compared to data for concrete, since there are no durability index tests available for waste derived bricks. The results obtained will provide an understanding of the sustainability of using waste in bricks over a long term.

6.1 Method

6.1.1 Preparation of test specimens

The method used was adopted from the 2018 Durability Index Testing Procedure Manual [10]. Figure 6.1 shows a coring drill coupled to a water-cooled diamond-tipped core barrel with a nominal internal diameter of 70 mm. A disc specimen was cored within the brick. After coring, the specimen was kept at room temperature for a maximum of 3 days before cutting. Then the specimen was cut using a diamond cutter to remove the excess material from the brick to achieve the desired dimensions. Typically, 5 mm was removed from the surface of the core and a thickness of 30 ± 2 mm of the test specimen was cut from the core. For the purpose of conducting durability tests, the specimens were kept in an oven at $50 \pm 2^\circ\text{C}$ for a minimum of 7 days and a maximum of 8 days.

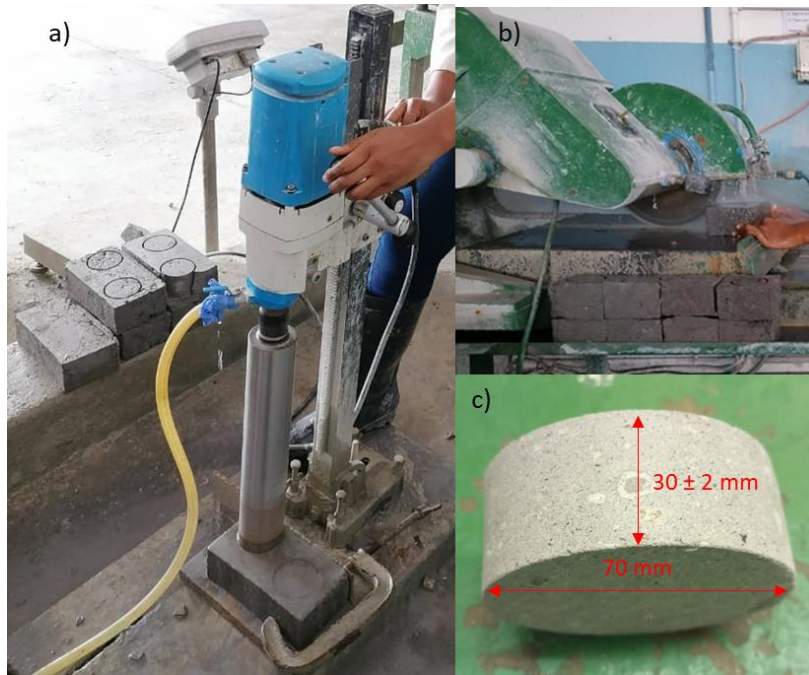


Figure 6.1: a) water-cooled diamond-tipped core barrel, b) water-cooled diamond cutter and c) cored specimen

6.1.2 Tests on brick specimens

6.1.2.1 Oxygen permeation index

The specimens were removed from the oven after drying and immediately placed in the desiccator and allowed to cool for 2 h. Then, their thickness and diameter were measured using a Vernier calliper accurate to 0.02 mm at 4 equal points around the perimeter of the specimen and an average of the readings was taken. With the exterior (test) face at the bottom, the specimen was positioned into the rigid sleeve and secured in the compressible collar (Figure 6.2). There were no obvious spaces between the test specimen's sides and the collar.

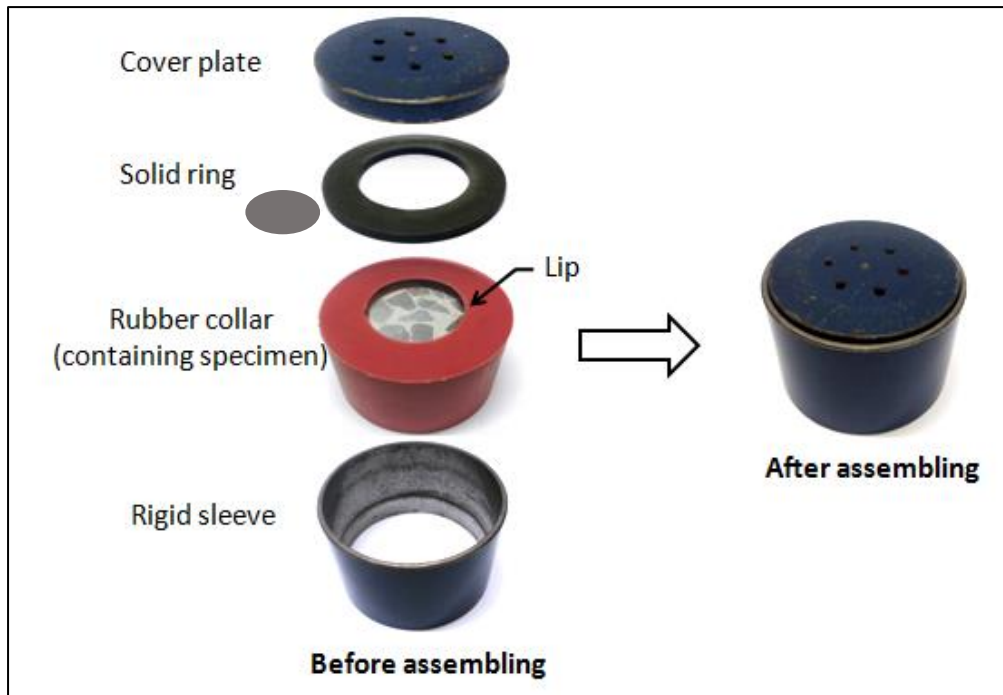


Figure 6.2: Specimen assembly parts for the permeability cell [10]

The sample, collar and rigid sleeve were placed in the permeability cell to cover the hole (Figure 6.3). The specimen was centred and tightened to ensure no gas leaked. The oxygen outlet was opened at a pressure between 100 -120 kPa for 5 sec to purge the test chamber. The permeability cell's outflow valve was closed. Next, the inflow valve was closed and the pressure was raised to 100 ± 5 kPa. Testing was stopped when the observed pressure drop reached 50 ± 2.5 kPa.

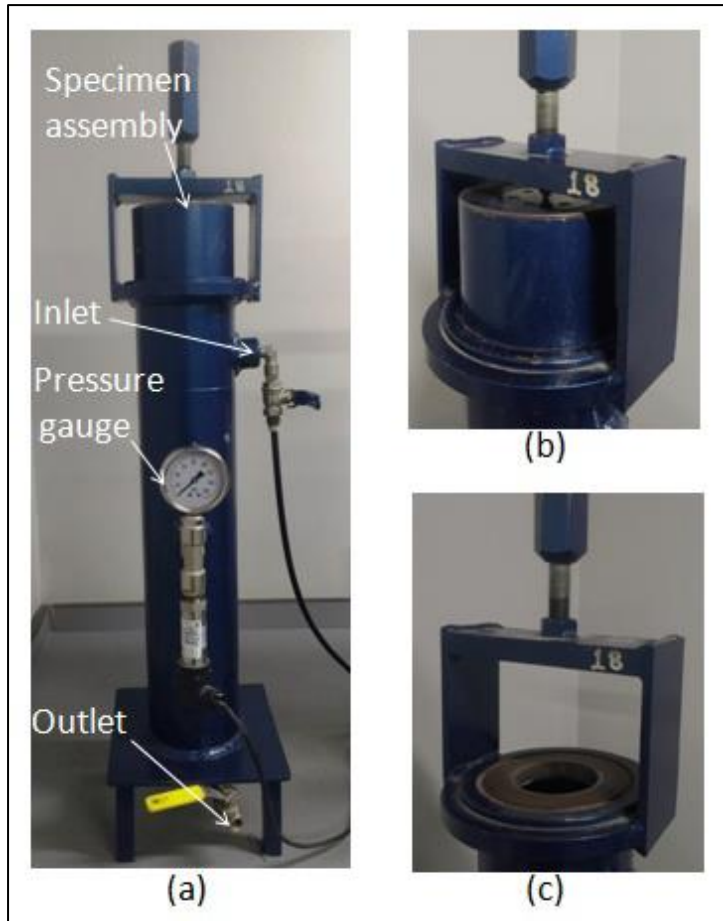


Figure 6.3: a) Permeameter setup, (b) a close-up of specimen assembly, and (c) cell without specimen assembly [10]

6.1.2.2 Water sorptivity and porosity test

One day prior to testing, a solution of calcium hydroxide (3 grams of $\text{Ca}(\text{OH})_2$ per litre of water) was made and kept at $23 \pm 2^\circ\text{C}$. Before being tested, the specimens were removed from the oven and allowed to cool in a desiccator. Using a Vernier calliper, their thickness and diameter were measured at four different locations around the perimeter and recorded to the nearest 0.02 mm. An average was then calculated. A piece of tape was used to seal the curved edges, and the dry mass was measured. The $\text{Ca}(\text{OH})_2$ solution was poured into a tray containing the specimens after it had been stacked with ten layers of paper towels. Two millimetres of the specimen were submerged in the solution to cover the bottom (Figure 6.4). After patting the specimens with a paper towel to remove excess solution, the specimens were weighed at 3, 5, 7, 9, 12, 16, 20, and 25 minutes. Following the process of weighing, the samples were subjected to a saturated vacuum of -75 to -80 kPa for a duration of 3 h 15 min. After that, the

Ca(OH)₂ solution was let to circulate inside the chamber, and the pressure was restored for an hour. After the specimens had been in the solution for 18 h, the pressure was finally removed, and they were weighed.



Figure 6.4: Sorptivity tray with specimens and Ca(OH)₂ solution

The amount of water or solution that penetrated the bricks was measured and used to calculate the water absorption and sorptivity of the bricks using the equations below. The values obtained gave an understanding of the durability of the bricks.

The porosity of the specimens was calculated using the following equation [6.1] [11]:

$$n = \frac{M_{sv} - M_{s0}}{Ad\rho_w} \times 100 \dots\dots\dots [6.1]$$

where:

M_{sv} is the vacuum saturated mass of the specimen in grams

M_{s0} is the mass of the specimen at time t₀ (start of the test) in grams

A is the cross-sectional area of the specimen in mm²

d is the average specimen thickness to the nearest 0.02 mm, in millimetres

ρ_w is the density of water in g/mm³

Sorptivity was calculated using the following equation [6.2] [11]:

$$S = \frac{Fd}{M_{sv} - M_{s0}} \dots\dots\dots [6.2]$$

where:

F is the slope of the best fit line in gram per square root of hour.

6.1.2.3 Chloride conductivity test

A 5 M solution of sodium chloride (NaCl) (2.93 kg in 10 L water) was made and kept at 23 ± 2 °C for a minimum of one day. Before being tested, the specimens were removed from the oven and allowed to cool in a desiccator. The specimens' dry mass was calculated and noted. The specimens were then placed in a saturated vacuum, and the procedures for water absorption were repeated with the exception of the NaCl solution. The plastic tubes (Luggin capillaries) were fitted with the specimens and then filled with a 5M NaCl solution. The anode and cathode parts of the cell were screwed into the central section. Finally, the voltmeter and ammeter were linked, and the DC power supply was adjusted until the capillary voltage (the voltage delivered across the specimen) was roughly 10 V (Figure 6.5). The ammeter and voltmeter were used to record the current and voltage readings simultaneously.

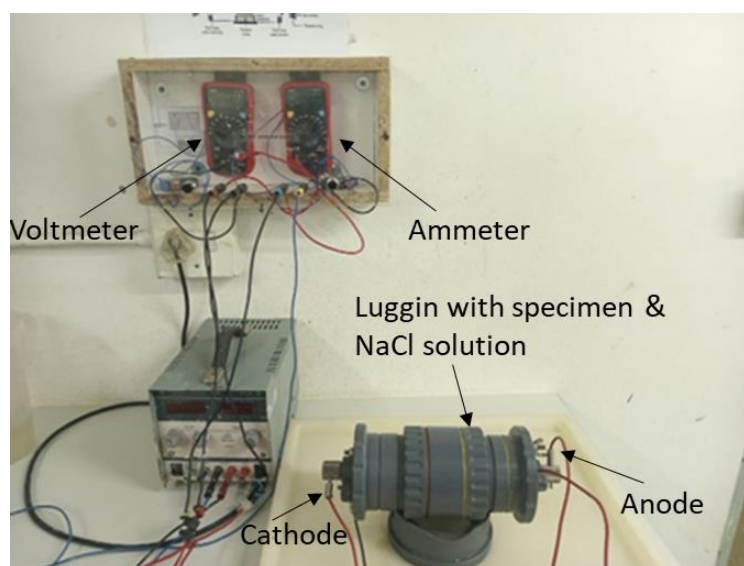


Figure 6.5: Chloride conductivity test setup

Chloride conductivity was calculated using the following equation [6.3] [12]:

$$\sigma = \frac{id}{VA} \dots\dots\dots [6.3]$$

where:

σ is the chloride conductivity of the specimen (mS/cm)

i is the electric current (mA)

d is the average thickness of specimen (cm)

V is the voltage difference (V)

A is the cross-sectional area of the specimen (cm²)

Porosity was calculated using the following equation [6.4] [12]:

$$n = \frac{M_s - M_d}{Ad\rho_s} \times 100 \dots\dots\dots [6.4]$$

where:

n is the porosity as a fraction of the volume of the specimen that is occupied with the solution, as a percentage (%).

M_s is the vacuum saturated mass of the specimen to in grams (g).

M_d is the mass of the dry specimen in grams (g).

A is the cross-sectional area of the specimen in (mm²).

d is the average specimen thickness in mm.

ρ_s is the density of salt solution (g/mm³).

6.1.2.4 Thermal deformation

The bricks were placed in a furnace for varied temperatures and times. Compressive strength tests were performed on the bricks. Further, they were observed to detect any deformities and length changes and to determine their coefficient of linear expansion.

The coefficient of thermal expansion was calculated using the equation [6.5] below [13]:

$$\alpha = \frac{\Delta L}{L \Delta T} \dots\dots\dots [6.5]$$

where:

α is the coefficient of thermal expansion (K^{-1})

ΔL is the change in length (m)

L is the length (m)

ΔT is the change in temperature (K)

6.1.2.5 Chemical attack

Different specimens were immersed in i) a 5% sulfuric acid solution, or ii) a 5% sodium sulphate solution, for 28 days and the physical changes and the compressive strengths recorded.

Corrosion resistance was calculated using the following equation [6.6] [14] :

$$CR = \frac{S_a}{S_n} \times 100 \dots\dots\dots [6.6]$$

where:

CR is the corrosion resistance

S_a is the compressive strength of the bricks immersed in acid, MPa

S_n is the compressive strength of bricks cured normally, MPa.

6.1.2.6 Efflorescence

Brick samples were immersed in tap water for 7 days according to the ASTM C67 method and observed for efflorescence after the water was evaporated [15]. The specimens, in which no difference was observed, were regarded as not-effloresced and those in which a difference was observed, regarded as effloresced.

6.2 Results and discussion

6.2.1 Oxygen permeability

Using a 70 mm diameter and 30 mm thick core that had been oven-dried at 50 °C and put inside a falling head gas permeameter, this technique assessed the pressure decay of oxygen. The OPI test assesses a cast composite's external surface's overall micro- and macrostructure [14]. The matrix's intrinsic structure determines permeability. It is particularly sensitive to cracks and macro-voids that serve as short-circuits for the penetrating gas. Consequently, the test is useful in identifying the level of interconnectivity of the pore structure, the existence of bleed gaps and channels, and the compaction state [16].

Figure 6.6 shows the OPI of bricks with a 0.05 and 0.1 wt.% CNT loading. The oxygen permeability test failed for the control and the 0.01 wt.% CNT bricks because these bricks were very porous (refer to Chapter 5). The OPI that was obtained was 10.2 and 9.1 (log scale) for 0.05 and 0.1 wt.% CNT loading respectively. The OPI values for cast concrete commonly range from 8.5 to 10.5 (on a log scale), with higher values indicating concrete of higher impermeability and potential of a higher quality [17]. It must be noted that the specimens were building bricks, which require a degree of permeability for binding with mortar unlike cast concrete. The 0.05 wt.% bricks had a higher OPI indicating a higher degree of impermeability than the 0.1 wt.% bricks. This was because of the densified microstructure due to the good dispersion of CNTs which filled the pores as compared to the 0.1 wt.% sample where the CNTs started to agglomerate and created voids (see section 5.3.5). However, the 0.05 wt.% bricks still had an acceptable OPI and can be regarded as durable. Furthermore, the bricks used contained fly ash which is also known to fill voids due to their spherical shape [8]. It has been reported that the incorporation of fly ash in concrete mixes improves the microstructure of composites and in polymers it fills the voids created during heating and melting [8]. In a study of geopolymer composites with fly ash, the OPI was found to be in the range of 9.5 log scale. Other composites of different mixes tested poorly in the OPI tests. This was attributed to the low rate of fly ash dissolution, resulting in low geopolymerization. As a result, a less dense binder of low strength was formed with poor durability index results [7].

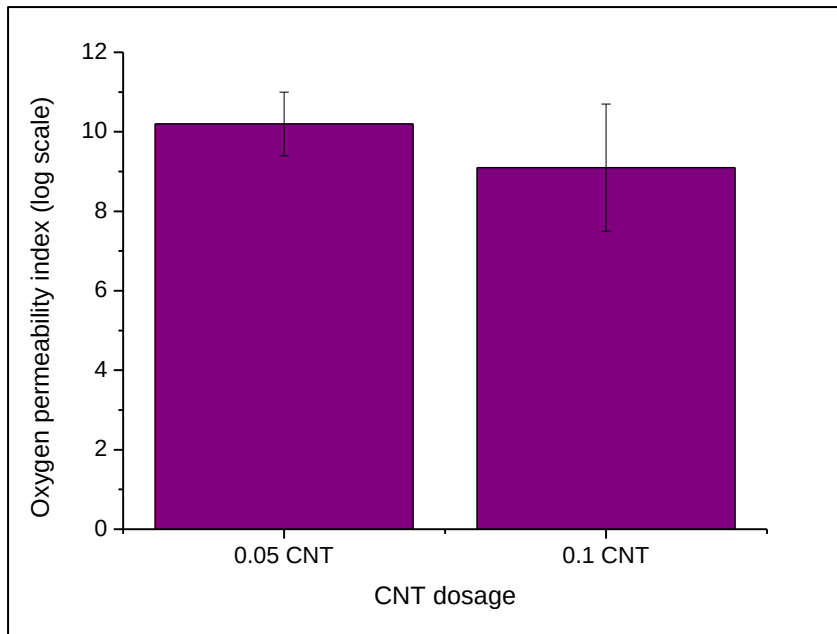


Figure 6.6: Oxygen permeability index of bricks containing varied amounts of CNTs

6.2.2 Water sorptivity and porosity

Sorptivity is the rate at which a porous material is penetrated by a wetting front under the influence of capillary forces. The pore geometry, including the orientation and connectivity, has an impact on this rate. The best bricks have a lower sorptivity value, which implies greater resistance to moisture infiltration [18]. Thus, bricks with a high-water absorption capacity are less durable. Porosity is not typically considered directly as a separate durability-related parameter; however, it has a great influence on the sorptivity of materials [19]. Figure 6.7 a) shows the water sorptivity index (WSI) of the bricks at different CNT dosages. It was observed that as the CNT dosage increased, the WSI decreased. This indicated an improvement in the durability, and thus, the quality of the bricks. The WSI decreased from 10.9 to 7.3 mm/vh on the addition of a 0.05 wt.% CNT dosage. However, the WSI increased for the 0.1 wt.% CNT bricks to 9.4 mm/vh. This was due to the agglomeration of CNTs at higher dosages which negatively affected the microstructure of the bricks. The control and the 0.1 wt.% had a higher error bar which could be attributed to an inhomogeneous matrix. According to the classification developed by Alexander for concrete materials, excellent concrete has a WSI of < 6 mm/vh, while good concrete values fall between 6 - 10 mm/vh. A value of 10 - 15 mm/vh is regarded as being associated with poor concrete and > 15 mm/vh is associated with very poorly constructed concrete [17]. This above values for concrete were used to give a measure

of the durability of the waste derived bricks. It was only the 0.05 wt.% bricks that can be regarded within the “good” classification, with the other bricks classified as ‘poor’ when correlated with values for concrete. However, it should be noted that, bricks do not require the level of compactness and resistance to moisture infiltration as does concrete. However, bricks with a high intolerance to moisture infiltration can be used as a measure for evaluating foundational brick structures.

Figure 6.7 b) and Table 6.1 show the average porosity of bricks at different CNT dosages after 28 days of curing. The porosity of the bricks decreased with an increase in CNT dosage from 5.19 %, to 3 % to 2.04 % for the 0, 0.01 and 0.05 wt.% CNT bricks respectively. This was due to the densified microstructure of the bricks upon the inclusion of CNTs, resulting in bricks that were less porous. This was a proportional relationship to sorptivity. However, similar to sorptivity, at 0.1 wt.% CNT dosages, the porosity increased to 2.43 % due to increased micro voids as a result of CNT agglomeration. A concrete is classified as excellent-good when the porosity is <10%, good-poor at 12%, and poor when it is >12%. According to the classification, the bricks were excellent-good [17]. The measure of porosity is an important measure as bricks lose moisture during the day (at high temperature) and reabsorb moisture at night (lower temperature). This phenomenon assists in maintaining the structure in terms of humidity and temperature. However, very porous bricks are susceptible to chemical attack and weathering. Thus, the performance of bricks is significantly affected by their porosity.

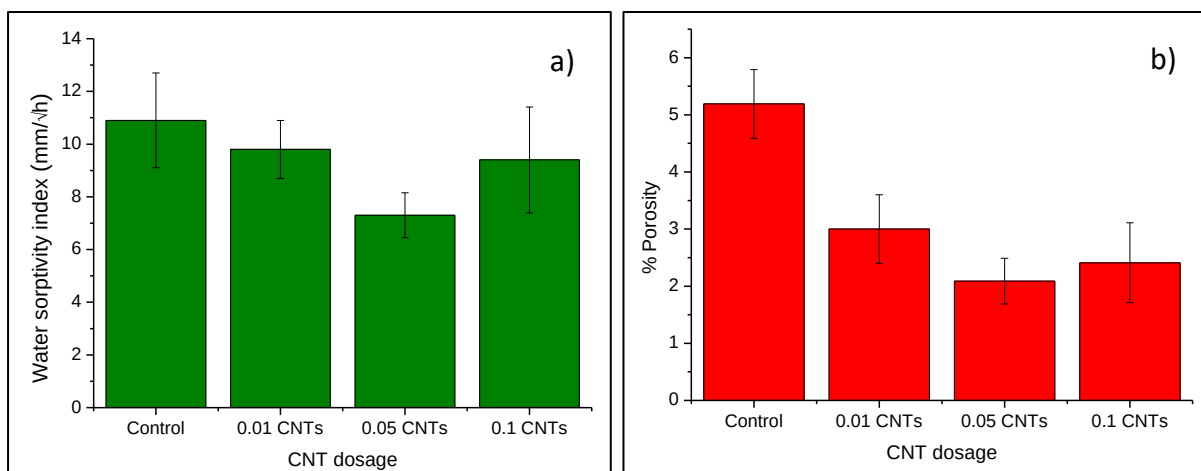


Figure 6.7: a) Water sorptivity index and b) porosity of bricks at various CNT dosages

Table 6.1: Porosity measurement of bricks

Material	Average ($M_{sv}-M_{s0}$) (g)	Area (mm ²)	Average thickness (mm)	Density of water (g/mm ³)	Porosity %
Control	0.0062	38.5	3.1	0.001	5.19
0.01 wt.% CNT	0.0037	38.5	3.2	0.001	3.00
0.05 wt.% CNT	0.0025	38.5	3.1	0.001	2.09
0.1 wt.% CNT	0.0030	38.5	3.2	0.001	2.43

6.2.3 Chloride conductivity

The concrete's resistivity to chloride intrusion is indicated by the chloride conductivity index (CCI). A lower resistance to chloride infiltration is indicated by a higher CCI value [20]. Concrete with a chloride conductivity of <0.75 mS/cm is regarded as excellent, 0.75-1.5 mS/cm as good, 1.5-2.5 mS/cm as poor and >2.5 mS/cm as very poor [21]. Figure 6.8 shows the chloride conductivity index of bricks at varied CNT dosages. The chloride conductivity of the bricks was reduced with an increase in CNT dosage, from 1.43 mS/cm for the control brick to 1.12 mS/cm, 0.88 and 0.78 mS/cm for the 0.01, 0.05 and 0.1 wt.% CNT dosed bricks, respectively. The reduction in CCI indicated an improved resistance to chloride ingress and thus durability. All the bricks fell within the "good" category, even though the CNT bricks exhibited improvements in chloride penetration. This was attributed to the improved microstructure of the bricks with CNTs. In a study testing geopolymers with different mixing ratios, geopolymers with optimum compressive strength were chosen due to their likelihood to have higher durability. The mixtures were 70–80 MPa high strength geopolymer concretes. There was no distinct pattern in the CCI values throughout the investigation. However, majority of the results fell within the poor durability category with values of >1.5 mS/cm [22]. The authors acknowledged that the durability index methods are mainly used for cement concretes. As such, the behaviour of the fly ash geopolymer concretes under CCI testing have not been fully understood. They concluded that since the CCI test is an electrical conductivity method, it is likely to be influenced by the solution ion fluxes which are very different in geopolymer concretes, as opposed to the Portland cement concretes [22]. Similarly, in this study, fly ash was used as an aggregate in the polymer bricks and their influence in durability

indexes as well as that of CNTs which are known to be conductive is not fully understood. Panagiota et al., [23] investigated the effect of CNTs on chloride penetration in cement mortars using a rapid chloride penetration test (RCPT). This was not a durability index test, however similar in that electric charge was allowed to pass through the nano-modified mortars to test their resistance to chloride ion penetration. It was found that all samples exhibited high chloride ion penetrability. Furthermore, the charge passed through the plain specimens was almost matching that passed through the nano-modified mortars. This finding suggested an insignificant effect of CNTs in the mortar [23]. Thus, more studies need to be undertaken to fully understand the effect of fly ash and CNTs particularly on chloride conductivity index as a measure of durability of building bricks.

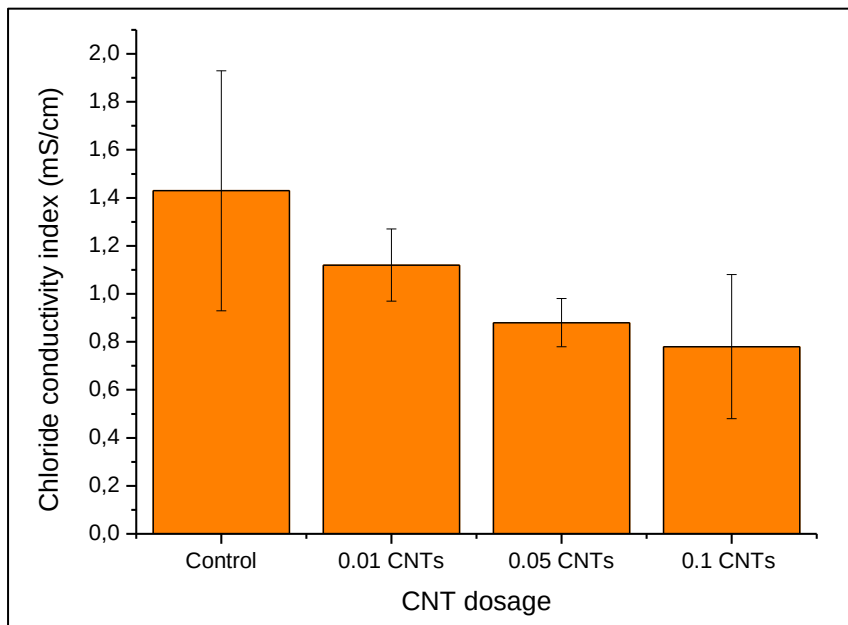


Figure 6.8: Chloride conductivity index of bricks with varied CNT dosages

6.2.4 Thermal resistance

The behaviour of structures during fire incidents can be better understood with the use of thermal analysis. The two most important parameters affecting thermal stability are density and porosity [24]. All materials expand and contract with changes in temperature [25]. Thus, knowledge of the thermal stability of materials is important, especially when plastic is used as a filler, which is known to have a high linear burning rate. The thermal tests were

performed for the control and the optimum CNT dosage of 0.05 wt.%, to study the effect of CNTs on the thermal stability of the bricks. Figures 6.9 and 6.10 show pictures of the control bricks and the 0.05 wt.% CNT bricks respectively after exposure to varied temperature (120, 220 and 320 °C) for 1 h. The bricks with and without CNTs were able to withstand a temperature of 120 °C without suffering structural deformation. This signified enhanced thermal stability as LDPE starts to melt at 105 - 115 °C [26]. It was evident that the coal fly ash aggregate caused the bricks to withstand temperatures that plastics alone could not stand. However, as the temperature increased to 220 °C the control bricks started to suffer structural deformities which were observed as uneven surfaces (bubbles) caused by the melting plastic. Furthermore, cracks were observed and the bricks started changing colour from grey to brown, which exhibited their burning.

It has been previously observed that the structural integrity of the bricks containing plastic holds very well up to 180 °C [14]. In that study the plastic bricks were made with sand as an aggregate. It was found that higher loadings of sand improved the thermal resistance of the bricks, due to the high thermal resistance of the sand [14]. Similar observations were made by Solomon et al., by examining thermal-resistance properties of plastic bricks every 30 mins. The bricks were made with sand and it was observed that high dense bricks showed higher thermal insulation and acoustic properties. The bricks were able to retain their structural integrity up to 180 °C, beyond that, the bricks weakened and fissures appeared. Thus, it was recommended that plastic bricks should not be used in fire susceptible regions [24].

In this study, temperatures of up to 320 °C were employed to study the effect of CNTs on the thermal stability of the bricks. It was observed that the structural integrity of the bricks was maintained for the 0.05 wt.% CNT bricks up to 220 °C. However, the colour of the bricks started changing from grey to brown. At 320 °C, the control bricks suffered structural disintegration with more uneven surfaces and bubbles being formed from the melted plastic. Cracks were also observed and a change in colour signified the loss of thermal stability of the brick. The 0.05 wt.% CNT brick showed cracks at 320 °C and exhibited a loss in structural integrity. However, the CNTs were able to stabilize the plastic within the brick and the bubbles were not as evident on the surfaces of the bricks as observed with the control bricks.

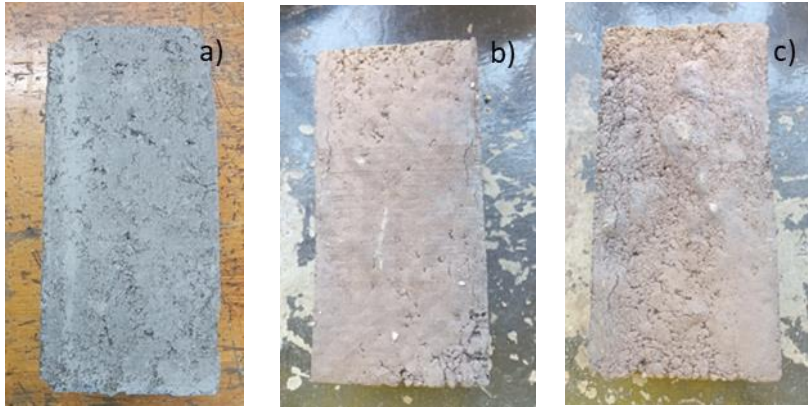


Figure 6.9: Control bricks after thermal exposure a) 120 °C, b) 220 °C, and c) 320 °C

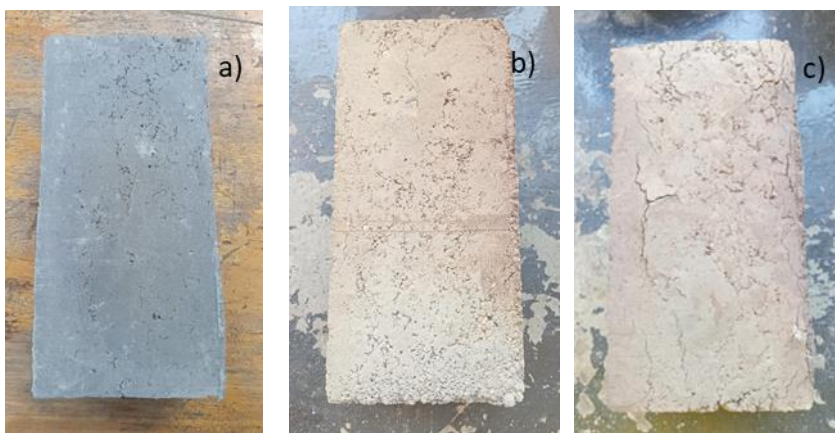


Figure 6.10: 0.05 wt.% CNT bricks after thermal exposure a) 120 °C, b) 220 °C, and c) 320 °C

The coefficient of linear expansion of the bricks (this measures the change in length at a specific temperature) was higher for the control bricks for all the different temperatures (Table 6.2). The control bricks had the highest coefficient of linear expansion of 9.7×10^{-6} at 120 °C (393.15 K), while the 0.01, 0.05 and 0.1 wt.% CNT bricks had a coefficient of linear expansion of $6 \times 10^{-6} \text{ K}^{-1}$, $2.4 \times 10^{-6} \text{ K}^{-1}$ and $3.6 \times 10^{-6} \text{ K}^{-1}$ at the same temperature respectively. The introduction of CNTs reduced the coefficient of linear expansion due to the improvements in the microstructure of the bricks as well as the thermal stability properties of CNTs and CFA. The 0.05 wt.% had the lowest change in length at different temperatures due to the compactness of the bricks as a result of well dispersed CNTs (see Chapter 5). The coefficient of linear expansion of the developed bricks was lower than that of concrete, which ranges between 10 and $14 \times 10^{-6} \text{ K}^{-1}$, and clay bricks, which range between 4 and $12 \times 10^{-6} \text{ K}^{-1}$ [27].

Table 6.2: Linear expansion of bricks

Sample ID.	Initial length (mm)	Change in length (mm)	Change in Temperature (K)	Linear expansion (K^{-1})
Control	223	0.8	369.15	9.7×10^{-6}
0.01	223	0.5	369.15	6.0×10^{-6}
0.05	224	0.2	369.15	2.4×10^{-6}
0.1	224	0.3	369.15	3.6×10^{-6}
Control	223	1.0	469.15	9.6×10^{-6}
0.01	223	0.6	469.15	5.7×10^{-6}
0.05	224	0.3	469.15	2.9×10^{-6}
0.1	223	0.3	469.15	2.9×10^{-6}
Control	223	1.1	569.15	8.7×10^{-6}
0.01	223	0.7	569.15	5.5×10^{-6}
0.05	225	0.5	569.15	3.9×10^{-6}
0.1	224	0.6	569.15	4.7×10^{-6}

6.2.5 Compressive strength after thermal exposure

Figure 6.11 shows the compressive strength of the control and 0.05 wt.% bricks after thermal exposure of 120, 220 and 320 °C. It was observed that the compressive strength decreased with an increase in temperature. This was due to the loss of structural integrity and the deterioration of the bricks upon high temperatures as shown in Figure 6.9 and 6.10. The compressive strength of the control bricks was 6.8, 5.2 and 3.2 MPa after thermal exposure to 120, 220 and 320 °C respectively. This was a significant loss in compressive strength from 11.9 MPa. The compressive strength of the 0.05 wt.% CNTs bricks was 19.4, 15.9 and 8.3 MPa after exposure to temperatures of 120, 220 and 320 °C respectively. The loss in compressive strength of the CNT-enhanced bricks was lower than that of the control bricks. This was attributed to the high thermal resistance properties of CNTs. Furthermore, the CNTs resulted in a compact structure which restricted the expansion and contraction of the bricks which usually results in cracks and weak spots. All the bricks, except the control brick at 320 °C (3.2 MPa), were within the recommended compressive strength for on-site buildings which requires a strength of 4 MPa. Similarly, Ayden et al., [28] studied the behaviour of cement bricks incorporated with RESIN8 (concrete additive made from waste plastic) subjected to fire conditions for an hour. The plastic replacement ratio was 0 - 50 wt.% at up to 420 °C. It was found that high plastic replacement ratios resulted in high smoke production, high mass loss and the disintegration of the bricks to form a black char surface. Significant material loss was observed in the 40% and 50% samples. Thus, it was recommended for safe buildings that will

ensure safe evacuation in case of fire, the optimum replacement ratio was set to be 5 - 10 wt.% [28].

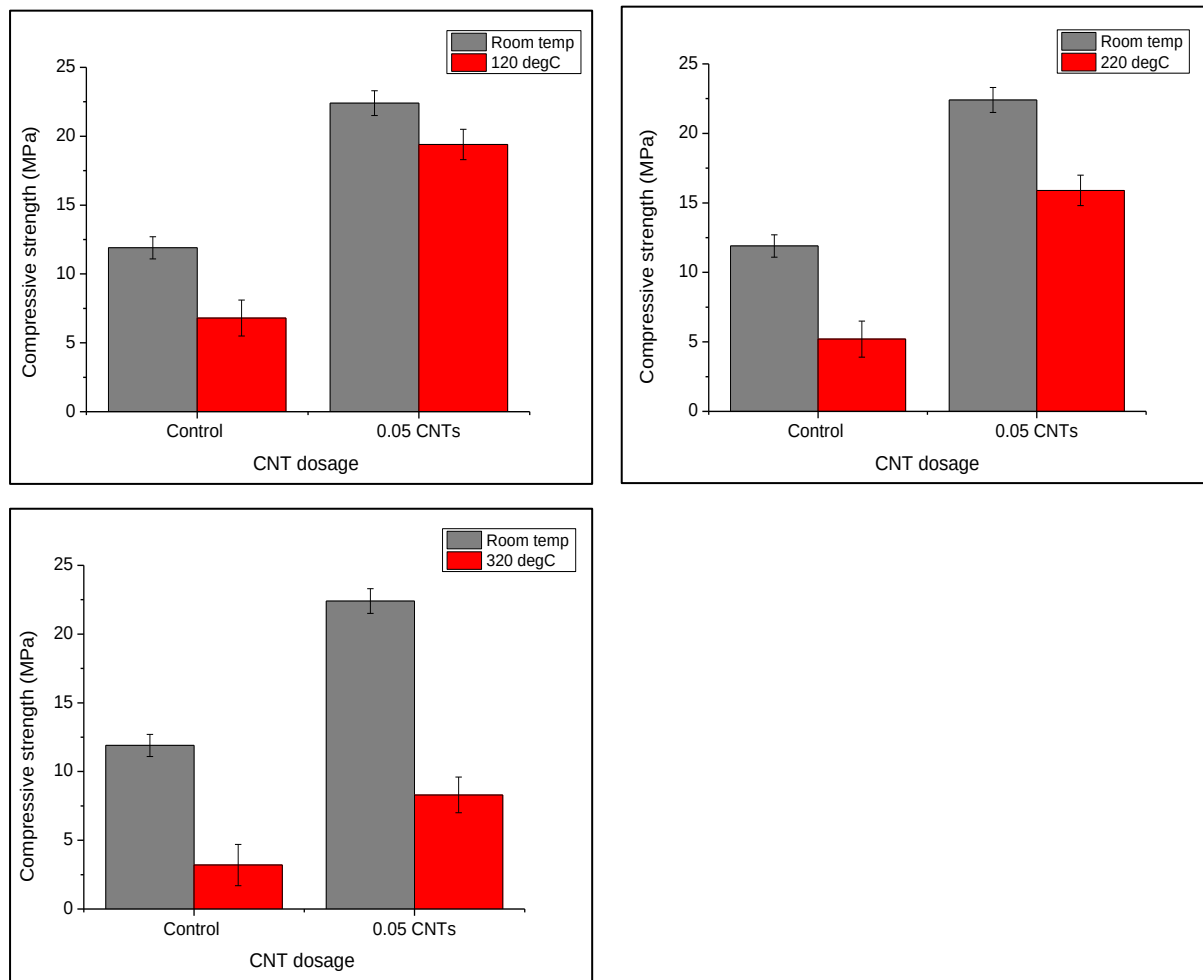


Figure 6.11: Compressive strength of bricks after thermal exposure

6.2.6 Chemical attack

The chemical attack tests (acid/base) were performed on control bricks and the 0.05 wt.% CNT bricks. To measure the chemical resistance of the bricks, compressive strength tests were performed on bricks exposed and not exposed to the chemicals (Table 6.3). Figure 6.12 shows the compressive strength of the bricks prior to, and after, chemical exposure. The compressive strength of the bricks was reduced upon chemical exposure due to the reduced microstructural integrity.

The acid resistance was 0.71% and 0.93% for the control and 0.05 wt.% CNT bricks respectively. In contrast, the base resistance was 0.81% and 0.97% for the control and 0.05 wt.% bricks respectively. The bricks showed more resistance to base attack than the acid attack. It has been reported that acidic conditions tend to show a larger strength reduction and higher increase in weight compared to tests in alkaline medium [29]. This is because sulfuric acid reacts to extract Al_2O_3 from the fly ash which weakens the bricks. Since, Al_2O_3 is a major constituent in fly ash (28.5%) (see Chapter 4), it results in a loss of strength of the bricks. In a study with fly ash and bottom ash incorporated clay bricks the corrosion resistance was found to be 0.8% and 0.77% under acidic and alkaline conditions respectively [29].

The CNT bricks were more resistant to the chemical attack than the control bricks. This was due to the improved microstructure of the CNT bricks. The reduced porosity limited the free movement of the chemicals within the structure of the brick. Similarly, other researchers have found that the performance of carbon nanomaterials such as CNTs, carbon nanofibers and graphene-enhanced composites reduce the transport of aggressive ions and harmful agents [30]. In another study, it was observed that the incorporation of 0.04 wt.% GO improved resistance to acid attack by enhancing both hydration and the microstructure of cement composites [3]. Wang et al., reported that an increase in MWCNTs loading increased chemical resistance to sulphate attack in concrete composites up to 0.1 wt.%. At higher dosages agglomeration occurred that led to weak bonds being formed with the hydration products. At a dosage of 0.05 wt.% (similar to the one used in this study) the authors found the sulphate resistance to be 0.98% after 50 days [31]. This is comparable to the data (0.97%) obtained in this study after 28 days of exposure.

Table 6.3: Chemical resistance of bricks

Sample ID	Compressive strength (normal) MPa	Compressive strength in acid MPa	Chemical resistance base %	Compressive strength in base MPa	Chemical resistance acid %
Control	11.9	8.4	0.71	9.6	0.81
0.05 wt.% CNT	22.4	20.7	0.93	21.9	0.97

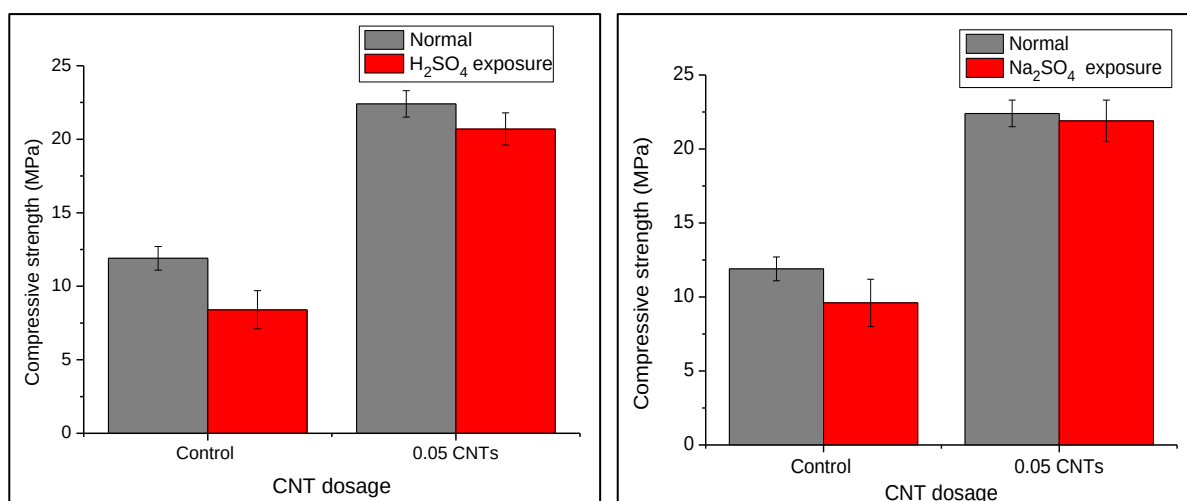


Figure 6.12: Compressive strength of bricks after chemical attack

6.2.7 Efflorescence

The dissolution of inorganic salts from waste materials like coal ash results in the formation of efflorescence or visible deposits which reduces the aesthetic quality of the building material [28]. It occurs most readily in porous concrete, near the concrete surface. Efflorescence is categorized as nil when no efflorescence is observed, slight if not more than 10% of an area is covered with a thin deposit of salt, moderate when 50% of the brick is covered, heavy when more than 50% area is covered and serious when there is heavy covering of salts together with powdering/ flaking of the brick [28].

The appearance of bricks before and after the efflorescence test showed that there were slight patches of white residue on all the bricks, as shown in Figure 6.13. The oxide that plays a key role in efflorescence is calcium oxide (CaO); while calcium carbonate (CaCO₃) can also be formed. In making the bricks, 85% of the material used was coal fly ash which had CaO at a concentration of 7.06% (see section 4.2.1.1). The CaO content from the coal fly ash could contribute to the minor efflorescence observed in the manufactured bricks. Subashi et al. used ceramic sludge with an 8.11% CaO content to manufacture bricks and no efflorescence was observed [32]. In another study tannery sludge, whose CaO content was 7.61 %, and with a binder material containing 50 % of fly ash (3.47 % of CaO), showed no significant efflorescence [33]. The minor patches observed in the bricks developed in this study are thus negligible and did not appear to have a negative structural or durability effect.



Figure 6.13: Control, 0.01, 0.05 and 0.1 wt.% CNT bricks before and after efflorescence tests

6.2.8 Research gaps in durability tests for waste-bricks

Significant literature for durability indexes was obtained for concrete rather than bricks which was the focus of the study. This is especially for oxygen permeability and chloride conductivity indexes. Typical durability tests that are usually performed on bricks are water absorption, efflorescence, chemical attack and mechanical strength [34]. These were reported in this study, and due to the use of unconventional materials (such as waste plastic as a binder rather than cement and CNTs as a reinforcement filler), more durability tests usually used to test concrete were undertaken. This was to expand understanding of the properties of the bricks especially since they possessed higher strength compared to conventional bricks. Bricks are not usually subjected to extensive durability tests as concrete due to their different applications. Concrete is required to be more resilient than bricks and be able to withstand more load in building and construction applications. However, similarities can be drawn in the type of raw materials used in both. There has been a growing trend in using waste materials such as fly ash, plastic, broken glasses, waste rubbles etc., in the developed of both concrete and bricks [35–38]. Thus, the durability indexes developed for concrete can find application in building bricks. However, requirement standards must be developed for bricks as they are not the same as for concrete.

6.3 Conclusion

The durability indexes and tests performed showed the effect CNTs on the bricks made in this study. It was observed that the CNT-enhanced bricks outperformed the control bricks. This is proposed to be due to an improved microstructure which made the bricks denser and less susceptible to losses in structural integrity. The control and 0.01 wt.% CNT bricks failed the

OPI test due to their low density and high porosity. In the WSI test, it was only the 0.05 wt.% bricks that fell within the “good” classification while the other bricks were in the “poor” classification. However, a level of water absorption is required for bricks, unlike cement concrete, in order to allow for binding with mortar during construction. All the bricks fell within the good category for the CCI test, albeit the CNT-enhanced bricks performed better than the control bricks. The thermal resistance tests showed that even in the presence of the plastic, which is highly flammable, that the bricks had acceptable properties. The control bricks started losing their structural integrity and strength at 220 °C. In contrast, the CNT bricks only became compromised at 320 °C. Furthermore, the CNT bricks showed more resistance to chemical attack in both acidic and basic media. However, the acidic medium resulted in more loss of compressive strength because sulfuric acid reacted to extract Al_2O_3 from the fly ash which weakened the bricks. Lastly, all the bricks exhibited some efflorescence, which had no effect on the structural or durability tests. The results obtained in this study shows the significance of adding CNTs in waste-derived bricks in improving their durability and thus sustainability.

6.4 References

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CHAPTER 7

ENVIRONMENTAL AND ECONOMIC SUSTAINABILITY OF CARBON NANOTUBE-REINFORCED BRICKS

7. Introduction

The construction industry plays a critical role in the sustainable development of many economies. It is a large-volume industry; thus, its environmental and economic impact is significant [1]. Building materials such as wood, reclaimed metal, natural stones and concrete bricks have been used to build structures [2]. However, bricks are still the most commonly used material. The traditional concrete bricks utilize Portland Cement (PC), which in its production emits large volumes of carbon dioxide (CO₂) [3]. The gas is known to be an environmental and health risk contributor. CO₂ impacts climate change and it directly affects crop production, food security, and human livelihood [4]. In recent years, there has been progress in developing alternative green building materials either from repurposing waste or using natural raw materials in an attempt to reduce CO₂ production [5]. Waste by-products such as coal ash and rice husk ash have been used as alternative alkali-activated binders in the construction industry [6]. This is to avoid the environmental impact associated with conventional binders (i.e. PC) in the development of bricks.

The utilization of coal fly ash (CFA) in the development of bricks is not without challenges. Although CFA is not classified as a hazardous waste, it contains some heavy metals (i.e. lead, arsenic, cadmium, copper) which may be toxic and pose a threat to health, if they leach into the environment in high enough concentrations [7]. The level of heavy metals present in CFA differs from each combustion thermal plant where it was produced. The heavy metals in CFA are normally found in trace levels (ppm) [8]. However, their quantification and leaching behaviour must be understood for their safe application.

The leaching of heavy metals in CFA found in bricks may infiltrate the soil and underground water used for irrigation purposes. This may pose threats to human beings and animals exposed to contaminated water and crops [9]. Some of the heavy metals at certain levels may be toxic to aquatic organisms, thus the leaching of heavy metals in CFA must be below set exposure levels.

The leaching of heavy metals is dependent on various factors such as pH, particle size, solid/liquid ratio and leaching time [10]. Consequently, the application of CFA bricks must be in areas that will not increase the leachability of heavy metals. It has been reported that in applications that rely on the pozzolanic properties of CFA, leaching of metals is unlikely since they are immobilized by the cement matrix [11].

With the aim to improve the properties of bricks for various applications, nanomaterials such as carbon nanotubes (CNTs) have been incorporated as reinforcement fillers. This has resulted in bricks with superior strength, thermal stability, lower water absorption and increased durability [12]. However, the potential leaching of CNTs from their application products has been a concern for several researchers. Thus, studies have investigated the potential health effects of CNTs and their toxicity [13]. Compared to micron-size carbon particles, the nano-size particles of CNTs have been found to pose respiratory health hazards upon inhalation [14]. However, engineered nanomaterials (ENMs) such as CNTs have been found to have a higher possibility of being released during their synthesis as opposed to their use in application products. This is because they are bound to the matrix of the composite and unlikely to leach to the environment [15].

The economic sustainability of building materials has a direct impact on the growth and advancement of a country. It informs the affordability and quality of the materials chosen for construction. Waste-derived bricks have become competitors of the conventional bricks in terms of their affordability, low carbon footprint, preservation of natural resources, reduced water usage, energy efficiency and their contribution towards a circular economy [16]. Affordable housing in sustainable development is mostly dependent on the cost of bricks. If the cost is reasonable, stakeholders will be more receptive to the adoption of alternate bricks. In this study, the environmental sustainability of a series of waste bricks was studied to (i) assess their environmental and economic sustainability in comparison to the conventional bricks and (ii) their ecotoxicity using *Daphnia magna* (*D. magna*) and *Raphidocelis subcapitata* (*R. subcapitata*) as test species.

7.1 Methodology

7.1.1 Sample preparation and leachate analysis

To simulate various environments, the metals (from the CFA) and CNTs in brick samples were leached in neutral, acidic and basic medium solutions to investigate their ecotoxicity in microalga (*R. subcapitata*) and aquatic organism (*D. magna*). The leaching procedure was adopted from the study by Gupta et al. [17].

The neutral leaching solution was prepared with tap water as it was a better representative of rainwater to which bricks are environmentally exposed. The acidic leaching solution was prepared using 0.5 ml glacial acetic acid in 1 L distilled water to make a 3.4 pH solution. A 9.3 pH solution was prepared with 20 g sodium tetraborate decahydrate in 1 L distilled water.

The control and 0.05 wt.% CNT bricks were first crushed using a ball mill and sieved with a 0.45 µm sieve. Portions of the crushed bricks (10 each) were added to 200 ml of the leaching solutions in Schott bottles. The samples were placed in a thermostatic shaker and shaken at 30±3 rpm for 18±2 h. The leachates were obtained by filtering the samples through a 0.45 µm glass microfiber filter and stored in a refrigerator at 4 °C for analysis. An inductively coupled plasma mass spectrometry (ICP-MS) was used to analyse the leachates for heavy metals, Ecotoxicity studies were performed on the leachates. Transmission electron microscopy (TEM) using a Tecnai FEI T12 instrument, coupled with energy dispersive spectroscopy (EDS) was used to determine the leachability of CNTs from the bricks.

7.1.2 Toxicity studies

7.1.2.1 *Raphidocelis subcapitata* growth inhibition test

The toxic effects of the leachates were investigated on *R. subcapitata* using a protocol described by Slabbert et al. [18] and used specifically for engineered nanomaterials (ENMs) in Lehutso et al. [19]. *R. subcapitata* was sub-cultured from the in-house stock at the Council for Scientific and Industrial Research Ecotoxicology Laboratory (Pretoria, South Africa).

Briefly, 10 mL of the stock cultures were regrown in 250 mL of 10% BG-11 medium at 25 °C and shaken on an orbital shaker (Labotech, Johannesburg, South Africa) at 100 rpm for six days under light (6000 lux). After the cultures had reached the exponential growth phase, 1 mL of the regrown cultures were transferred to 24 Eppendorf tubes (Inqaba Biotech, Johannesburg, South Africa) and centrifuged for 10 minutes at 11,000 rpm to create the experimental inocula. After discarding the supernatants, the algal cells were again dispersed in 100 µL of BG-11 media, vortexed for 30 seconds, centrifuged for 8 minutes at 11,000 rpm, and the supernatant was extracted. The procedure was carried out twice. The density of the algae and the total amount of algal culture needed for the entire test were calculated in accordance with guidelines of Helena et al. [20]. The 72-hour toxicity experiments were conducted at 25 °C, shaken at 100 rpm, and under 6000 lux of light as defined Slabbert et al. [18]. Cell density was evaluated using a microplate reader (FLUOstar Omega, BMG, Germany) set to 684 nm at times 0 and 72 hours. A 96-well plate was filled with 100 µL of the sample test for this measurement. Using non-linear regression with a 95% confidence interval, the 72-hour EC₅₀ (growth inhibition) was determined (GraphPad Prism Software v9, GraphPad Software Inc., Massachusetts, USA).

7.1.2.2 *Daphnia magna* acute immobilisation test

For the effects on *D. magna*, a modified and miniaturised OECD Acute Daphnia Immobilisation Test (TG 201) reported by Grintzalis et al. [21] was employed. Typically, *D. magna* cultures used were obtained from a continuous in-house stock at the Council for Scientific and Industrial Research Ecotoxicology Laboratory (Pretoria, South Africa). The cultures of *D. magna* were housed in an aerated water tank (2.5 L) maintained at 18 °C at a 16:8 h light: dark cycle. For the acute immobilisation test, cohorts of five *D. magna* neonates (≤ 24 h old) were added to a 24-well plate with 2 mL exposure medium in each well; nominal concentrations used ranged from 0% to 50% with four replicates each. The exposure was carried out over 48 h with immobilisation assessed every 24 h; the organisms were considered immobile if there was no movement within 15 seconds of gentle agitation. The EC_{50s} were determined using non-linear regression at 95% confidence interval in GraphPad prism v9 software (GraphPad Software Inc., Massachusetts, USA). The test results were considered valid if the immobilisation was $\leq 10\%$ in the controls.

7.2 Results and discussion

7.2.1 Environmental impact

The materials consumed during the production of bricks are shown in Table 7.1. The data is from a study performed by Maaze et al., [22] based on bricks with dimensions of 230 × 110 × 75 mm. The bricks produced in this study were similar, with dimensions of 220 × 105 × 70 mm (see section 5.1). The production of bricks has an environmental impact which must be considered for their sustainability. Studies have analysed global warming potential, fossil resource scarcity, water depletion, mineral resources scarcity, terrestrial acidification, ozone formation and freshwater eutrophication as some of the indicators of the environmental impact of bricks [22]. The conventional bricks have a high environmental impact due to their use of non-renewable resources and their production processes which require the use of energy and water.

Studies have shown that clay-fired bricks were the highest consumer of non-renewable resources (Table 7.1). The main component was clay which accounted for 3.5 kg per brick. The harvesting of these resources (i.e. clay, sand, stones) in large volumes results in ecological degradation. In a study conducted by Asante-Kyei et., [23] it was discovered that one of the main causes of pollution was the clay harvesting locations' proximity to river bodies. Moreover, the harvested areas were not reclaimed, trapping household animals and acting as a mosquito breeding ground [23].

In the clay brick production process, both the drying and firing stages are energy intensive. Drying is performed at 1000-1200 °C and can take up to 40-50 h. The firing process depends on the type of furnace used and can be operated at up to 1400 °C [24]. The processes consume energy and result in the release of GHGs that pollute the air and could lead to global warming. The clay bricks release an average of 0.41 kg of carbon dioxide per brick [25]. Rice et al., conducted a life cycle assessment study of clay bricks from the cradle-to-gate phases for the Clay Association of South Africa. It was found that the clamp kiln was the most used furnace for firing the bricks. The resources used were 0.03067 kg coal, 0.00925142 kWh electricity and 0.00076 L of diesel per kg of bricks [26].

The second highest natural resource consumer was the fly ash cement brick (Table 7.1) which did have a resource saving compared to the conventional cement bricks without fly ash. Producing 1 kg of OPC requires 0.006–0.013 kg of fuel oil or equivalent and about 0.11 kWh of electricity. Furthermore, every kg of cement releases 0.0009–0.001 kg of carbon dioxide [27]. Thus, the fly-ash cement bricks saved 2.73 kg (210x0.013 kg) of fuel, 23.1 kWh electricity and 0.21 kg of CO₂ emission per 100 bricks produced. Fly ash saved on the resources and reduced the negative environmental impact of cement. The recycled concrete waste (RCW) and recycled waste brick (RWB) geopolymers (Table 7.1) were even more resource saving due to the use of recycled materials. The only virgin materials used were alkali activators (NaOH and Na₂SiO₃). The data presented shows that when natural resources are replaced with waste products, the more the resources are saved, which in turn will reduce the environmental impact.

In this study, fly ash was the largest added component in the bricks, accounting for 85% and the rest being waste plastics and a small quantity (0.05%) of CNTs as a reinforcement filler (see section 5.3.1). The only synthesized material used was CNTs in small quantities. The production of CNTs used in this study required feedstock (ferrocene, toluene, nitric acid and nitrogen), and the process was performed at 850 °C for 30 min (see section 3.3.1). The carbon yield (CNTs) was high, which meant the process did not result in a lot of by-products/waste. However, many studies have shown that CNTs made using natural carbon feedstock (i.e. olive oil, rice straw, coconut oil, camphor) and renewable energy sources [28] can further reduce the negative environmental impact of the use of CNTs in the application of bricks as reinforcers. The brick manufacturing process was not as energy intensive as the conventional brick manufacturing processes. The energy required was for melting the plastic, mixing and compacting the bricks. The high energy used for drying and firing the bricks was saved because the bricks were sun dried. It was a quick process because of the high settling rate of the polymer composites. The bricks were produced without water and that aided sustainability considering the global water scarcity challenges. The total resource saving was 336 kg per 112 bricks produced. Even though not quantified, there was also an energy saving from the production process, reduced CO₂ emission and environmental remediation by repurposing waste.

Table 7.1: Inputs for brick manufacturing

Material consumed	Fired clay brick	Fly ash cement brick	Geopolymer fly ash brick	Geopolymer RCW brick	Geopolymer RBW brick	CNT-reinforced waste brick (this study)
Clay (kg)	350	-	-	-	-	-
Bagass (kg)	35	-	-	-	-	-
Sand (kg)	19	105	175	175	175	-
Coal powder (kg)	120	-	-	-	-	-
Fly ash (kg)	-	210	175	-	-	285
OPC (kg)	-	35	-	-	-	-
NaOH flakes (kg)	-	-	5.14	5.14	5.14	-
Liquid Na_2SiO_3 (kg)	-	-	50	50	50	-
Tap water (kg)	90	70	15	15	15	-
Recycled concrete waste (kg)	-	-	-	175	-	-
Recycled brick waste (kg)	-	-	-	175	175	-
Recycled plastic (kg)	-	-	-	-	-	50
CNTs (g)	-	-	-	-	-	168
Resource saving (kg)	0	210	175	175	350	336
No. of bricks produced	100	108	106	100	103	112

*RCW: recycled concrete waste, RWB: recycled waste brick

7.2.2 Economic sustainability

Table 7.2 presents the cost analysis of raw materials used to produce different types of building bricks. The data was sourced from recent literature (2020-2023) because pricing is time sensitive. These findings were from countries such as Malaysia, France and India as recent data was not available for South Africa. Cost variations were expected for different countries because of the availability of raw materials, regulations, standard of living, etc. However, the raw materials and quantities used especially for conventional bricks are standard. The cost analysis excludes the cost of other inputs in brick production such as water, energy, labour, transportation, equipment and maintenance which will need to be considered

in costing and pricing. These vary significantly e.g., the energy cost depends on the type of energy used such as coal powered, solar powered and gas.

Table 7.2: Cost analysis of raw materials per brick in \$

Raw material	Cement brick [29]	Clay brick [30]	Clay- geopolymer [31]	Fly-ash geopolymer [32]	CNT reinforced waste bricks (this study)
Clay	-	0.019	0.017	-	-
Cement	0.21	0.00	-	-	-
Sand	0.01	0.01	0.03	0.042	-
Gravel	0.01	-	-	-	-
Coal powder		0.06			
Alkali activators (NaOH & Na ₂ SiO ₃)	-	-	0.083	0.12	-
Iron chip	-	-	-	0,00042	
Ground granulated blast slag	-	-	-	0.01	
Fly ash	-	-	0.00	0.00048	0.00
Plastic	-	-	-	-	0.012
CNTs	-	-	-	-	0.079
Total	\$0.23	\$0.089	\$0.13	\$0.17	\$0.091

The data presented in Table 7.2 indicates that cement bricks were the most expensive (\$0.23 per brick) to produce in terms of the raw materials used, followed by fly-ash geopolymers, clay-geopolymers. The CNT-reinforced waste bricks produced in this study (and clay bricks) were the least expensive, at \$0.17, \$0.13, \$0.091 and \$0.089 per brick respectively. However, the Clay Brick Association estimates that the energy costs are 40% of the total clay brick production costs. Thus, the cost of energy increases the total cost per brick, especially for clay bricks which require high energy during the drying and firing process.

In this study, the fly ash was collected from Eskom (South Africa's power utility) at no cost. A small cost came from the waste plastic as it was sourced from a waste management company that cleaned and sorted it. The cost for 1 kg of plastics was R0.50 (\$0.026) and for every 3 kg brick, 15% (0.45 kg) was used, thus, the cost of plastic per brick was R0.23 (\$0.012). For every 3 kg brick, 0.05% of CNTs was used which was 1.5 g per brick. The cost of CNTs production was calculated as R 1000 (\$52.86) per kg. Thus, the price per brick was R 1.74 (\$0.091). It is noteworthy that the bricks can be produced from a lower CNT dosage (e.g. 0.01 wt.%) which

also showed improved properties from the bricks without the CNTs (see Chapter 5). The choice of CNT loading must be related to the desired application. If the application is low-end and does not require the superior properties (such as high mechanical strength) of the 0.05 wt.% dosage, then a lower loading can be used. This can reduce the price of production significantly. For example, the price of production (only considering the raw materials) if using a 0.01 wt.% loading can reduce the cost from R1.74 (\$0.091) to R 0.54 (\$0.028).

In Figure 7.1, the compressive strength of the bricks for different CNT dosages was compared with the cost per brick. The relationship was directly proportional, with an increase in CNT loading resulting in higher compressive strength and higher cost. The cost of raw materials can increase from \$0.012-\$0.28 with an increase of 0-0.1 wt.% CNT dosage respectively. In a geopolymers brick feasibility study, it was found that 70% of the cost of brick manufacture came from the use of alkali solutions. The cost increased from \$0.067 for pressed fly ash brick to \$0.11 for geopolymers bricks [32]. However, similar to CNT reinforced bricks, it was observed that the price of the bricks could be reduced by optimizing the raw material that had the highest price contributor, in their case the liquid to solid ratio.

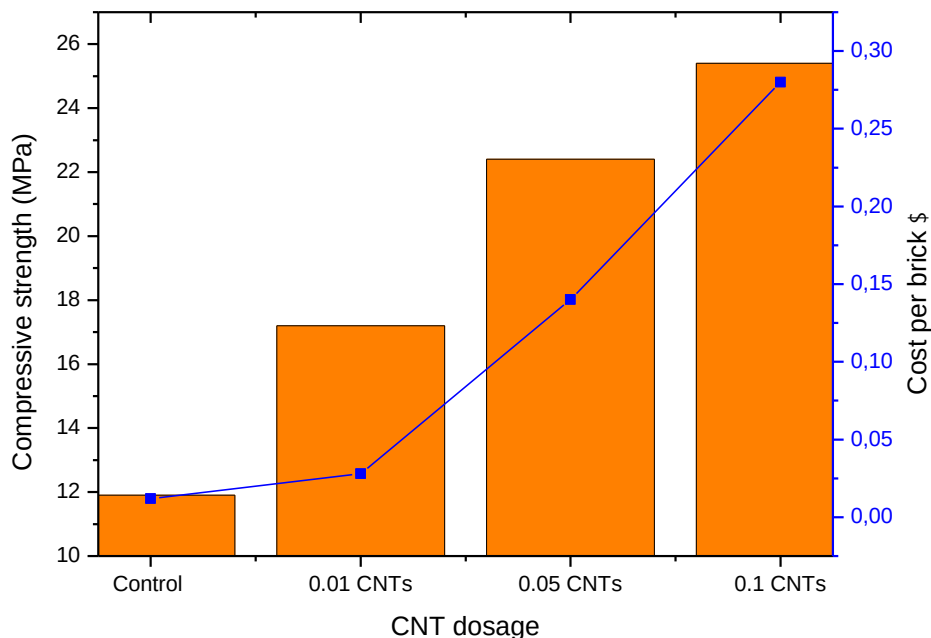


Figure 7.1: Compressive strength of the bricks at different CNT loading vs cost per brick

7.2.3 Elemental analysis of heavy metals in leachates

CFA used in applications is not in a powder form but is used as an aggregate in building bricks, of which the matrix remains bound unless they are demolished. Accordingly, the leaching of heavy metals would be lower in solid bricks than the crushed samples. Nevertheless, it is important to understand the entire life-cycle of the product from its production, usage and end of life for its safe application and to determine its sustainability. For this reason, the studies below have been carried out using powdered materials

Tables 7.3 and 7.4 presents the elemental analysis of the pristine and CNT brick leachates under various conditions respectively. The results were compared with the South African National Standards (SANS10234) and the World Health Organization (WHO) proposals [33,34]. Furthermore, the results were compared with the EC_{50} of *R. subtapitata* and *D. magna* reported by Hasawi et al., [35] and Okamoto et al.,[36] respectively for the CFA leachate ecotoxicology. The ecotoxicology results are discussed in the next section.

In both the brick samples, the leaching of heavy metals was high under acidic conditions (pH 3.4) compared to the neutral (pH 7) and basic conditions (pH 9.3). Similar results were obtained by Sarode et al., [37] This arises since metal solubility generally decreases with increasing pH [37]. In acidic pH, the high concentration of H^+ destroys the amorphous aluminium silicate and exposes heavy metal ions to leaching. In neutral conditions, the concentration of H^+ is decreased and hence, the structure of the aluminosilicate is more stable which decreases the leaching of heavy metal ions [38]. A study has found that leaching solutions of CFA were basic, indicating that CFA can release alkaline components and alter the pH of the solution. Furthermore, increased pH levels cause the alkali components to stay in the leaching solution, and the produced OH^- precipitates with the heavy metal ions, lowering the concentration of those metals [39].

In neutral leaching conditions, for both the pristine and CNT brick leachates, As, Cr, Mo, V and Cd were leached above the leaching concentration threshold (LCT0). However, none of the metals were above the LCT1, meaning the waste could be classified as moderately toxic in such leaching conditions [33]. In acidic conditions, for both the brick samples, As, Cr, Mo, V, Cd, Zn and Mn were leached above the LCT0. The leaching of As and Cd in the pristine brick was high and above the LCT3. This meant that the leachate was toxic and not safe to be

released to the environment. In basic conditions using the pristine brick leachate, only As and Cd were above the LCT0. Lastly, As, Cr, Mo and V were above the LCT0 for the CNT brick leachate under basic conditions.

The leaching of heavy metals from the bricks is an environmental and health concern. However, it is worth noting that the leaching procedure of the bricks involved crushing them to a particle size below 0.45 μm . This exposes a larger surface to the leaching of heavy metals. Volatile metals (metals that easily convert to vapour under moderate heat) such as Zn, Pb, Cu and Cd have been found to be more abundant in finer particles with the potential ecological risk increasing with a decrease in particle size [38]. In this study, Zn and Cd were found to be above the threshold limit and that could be attributed to the fine particle size used for leaching.

There are many strategies to prevent the leaching of heavy metals from CFA of which repurposing into building materials is one them. Other strategies involve chemical stabilization using alkaline solutions to neutralize the acidic components in CFA and also thermal treatment to reduce leachability. In a study, a process called flash Joule heating (FJH) was used for the removal of heavy metals from CFA. The FJH uses an electric pulse to ramp up the temperature to $\sim 3000\text{ }^{\circ}\text{C}$ within one second. This, aids in the evaporative removal of As, Co, Ni, and Pb with removal efficiencies of 70-90%. This resulted in reduced heavy metal leakage under acid leaching for CFA application in Portland cement [40].

Table 7.3: Leaching of heavy metals from pristine bricks under different conditions

Heavy metals	Threshold limits							Ecotoxicology	
	Neutral (mg/l)	Acid (mg/l)	Base (mg/l)	LCT0 (mg/l)	LCT1 (mg/l)	LCT2 (mg/l)	LCT3 (mg/l)	LC ₅₀ <i>R. subcapitata</i> (mg/l)	LC ₅₀ <i>D. magna</i> (mg/l)
Pb	0.008	0.0025	0.0036	0.01	0.5	1	4	5	0.29
As	0.5	6.2	0.5	0.01	0.5	1	4	4	2.4
Co	0.09	0.3	0.005	0.5	25	50	200	0.06	0.71
Cr	0.2	0.08	0.001	0.05	2.5	5	20	0.3	0.13
Cu	0.9	0.8	0.0008	2	100	200	800	0.3	0.013
Mo	0.5	1,1	0.0005	0.07	3.5	7	28	nd	1 500
V	0.5	3.8	0.002	0.01	0.5	1	4	nd	1.2
Cd	0.01	2.3	0.008	0.003	0.15	0.3	1.2	0.05	0.0036
Ni	0.3	0.18	0.003	5.01	3.5	7	28	0.3	0.65
Zn	0.5	8.0	0.005	5	250	500	2000	0.1	0.72
Mn	0.1	3.1	0.002	0.5	25	50	200	nd	9.3

Pb: lead, As: arsenic, Co: cobalt, Cu: copper, Mo: molybdenum, V: vanadium, Cd: Cadmium, Ni: nickel, Zn: zinc, Mn: manganese. *Values highlighted in orange and the LC₅₀ highlighted in red are for metals above the threshold limit, nd: not determined

Table 7.4: Leaching of heavy metals from CNT bricks under different conditions

Heavy metals	Threshold limits				Ecotoxicity				
	Neutral (mg/l)	Acid (mg/l)	Base (mg/l)	LCT0 (mg/l)	LCT1 (mg/l)	LCT2 (mg/l)	LCT3 (mg/l)	LC ₅₀ <i>R. subcapitata</i> (mg/l)	LC ₅₀ <i>D. magna</i> mg/l
Pb	0.009	0.001	0.009	0.01	0.5	1	4	5	0.29
As	0.6	3.2	2.1	0.01	0.5	1	4	4	2.4
Co	0.06	1.1	0.06	0.5	25	50	200	0.06	0.71
Cr	0.3	0.1	0.3	0.05	2.5	5	20	0.3	0.13
Cu	0.8	1.7	1.6	2	100	200	800	0.3	0.013
Mo	0.5	0.8	0.3	0.07	3.5	7	28	nd	1 500
V	0.6	2.8	0.7	0.01	0.5	1	4	nd	1.2
Cd	0.07	0.02	0.002	0.003	0.15	0.3	1.2	0.05	0.0036
Ni	0.07	0.2	0.002	5.01	3.5	7	28	0.3	0.65
Zn	1.1	3.5	0.02	5	250	500	2000	0.1	0.72
Mn	0.06	1.5	0.1	0.5	25	50	200	nd	9.3

7.2.4 Ecotoxicology

7.2.4.1 *Raphidocelis subcapitata*

Figure 7.2 shows the growth inhibition of the *R. subcapitata* (microalgae) after 72 h of exposure in different media. The 72h-EC₅₀ (effect concentration on 50% of the test species after 72 h) at a neutral pH was 2.84% and 10.80% for the study under basic condition. The study was not conducted under acidic conditions. The EC₅₀ was not determined in an acidic pH due to the high potency of the leachate. Table 1 shows that in neutral conditions, Co (0.09 mg/l), Cu (0.9 mg/l), Zn (0.5 mg/l) were higher than the EC₅₀ for *R. subcapitata* of 0.06 mg/l, 0.3 mg/l and 0.1 mg/l for the heavy metals respectively. In acidic medium, As, Co, Cu, Cd and Zn were higher than the EC₅₀ of the microalgae. Lastly, in basic medium no heavy metal was found in levels above the EC₅₀ for the microalgae. The microalgae were affected by pH because pH affects the availability of CO₂ and nutrients, which are essential for the species' survival. In this study the optimum growth pH for the microalgae is 7.5 [41] and in basic conditions it was 9.3.

At the highest leachate concentration, the growth inhibition was 65%, 88% and 55% for the neutral, acidic and basic leachates respectively. As shown from the ICP results (Tables 7.3 and 7.4), the leaching of heavy metals increased with a decrease in pH. Hence the basic leachate showed a higher EC_{50} due to the lower levels of heavy metals compared to the other leachates. These results showed a high toxicity of the leachates to the microalgae even at low concentrations. The growth inhibition of the neutral leachate (Figure 7.2a) was high at low concentrations but plateaued, which showed that even higher concentrations of the leachate had a similar effect on the microalgae. In acidic and basic medium, the growth inhibition increased with an increase in leachate concentration.

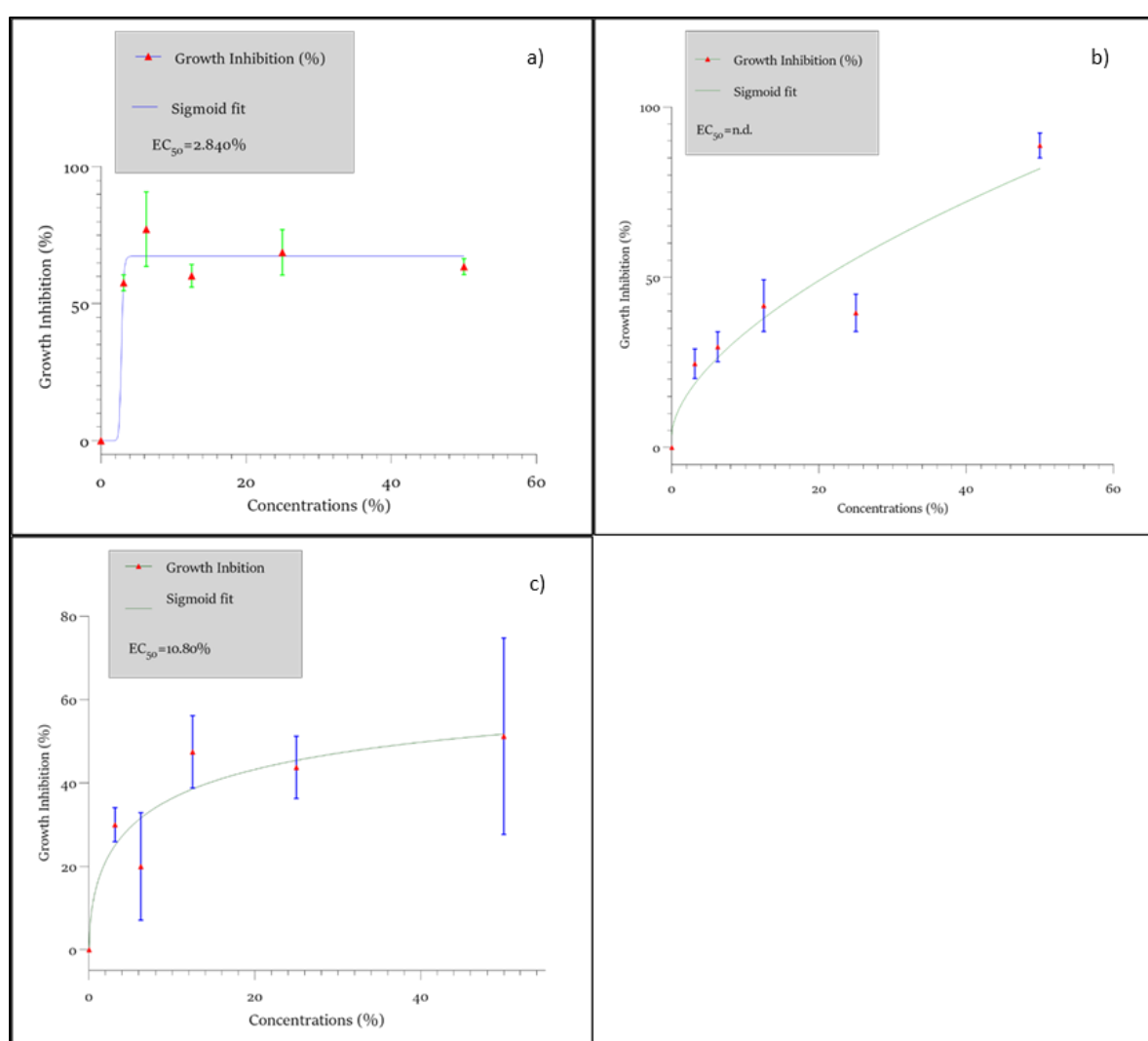


Figure 7.2: Growth inhibition of algae exposed to pristine brick leachates in a) neutral, b) acidic, and c) basic medium

Figure 7.3 represents the growth inhibition of microalgae exposed to neutral, acidic and basic media of CNT brick leachates. The EC_{50} was only determined for the acidic medium and found to be 3.7%. The toxicity of the leachate to the microalgae was high under the various conditions. Table 7.4 shows that in neutral conditions, Cr, Cu, Cd and Zn were above EC_{50} of the microalgae. In contrast, in acidic medium, only Cu and Zn were above the EC_{50} and lastly, in basic conditions only Cu was above the EC_{50} of the microalgae.

At the highest leachate concentration of 50%, the growth inhibition was 85%, 60% and 85% for the neutral, acid and base leachates respectively of the CNT containing samples. The effect of the CNTs on the microalgae was inconclusive because the TEM-EDS results showed that the CNTs leached in basic medium. However, the growth inhibition of the test species varied significantly even in neutral and acidic conditions. This was attributed to the complex leachate matrix which contained several metals that might have formed complexes with metals at different environmental conditions (e.g. pH) and affected the growth of the microalgae. The effect of graphene oxide (carbon nanomaterial) was studied on the *R. subcapitata*. It was found that carbon nanoparticles can cause indirect toxicity effects such as shading due to aggregation in the algal medium, decreasing chlorophyll activity and inhibited growth. Furthermore, their opaque nature can decrease the availability of light and affect algal photosynthesis [42].

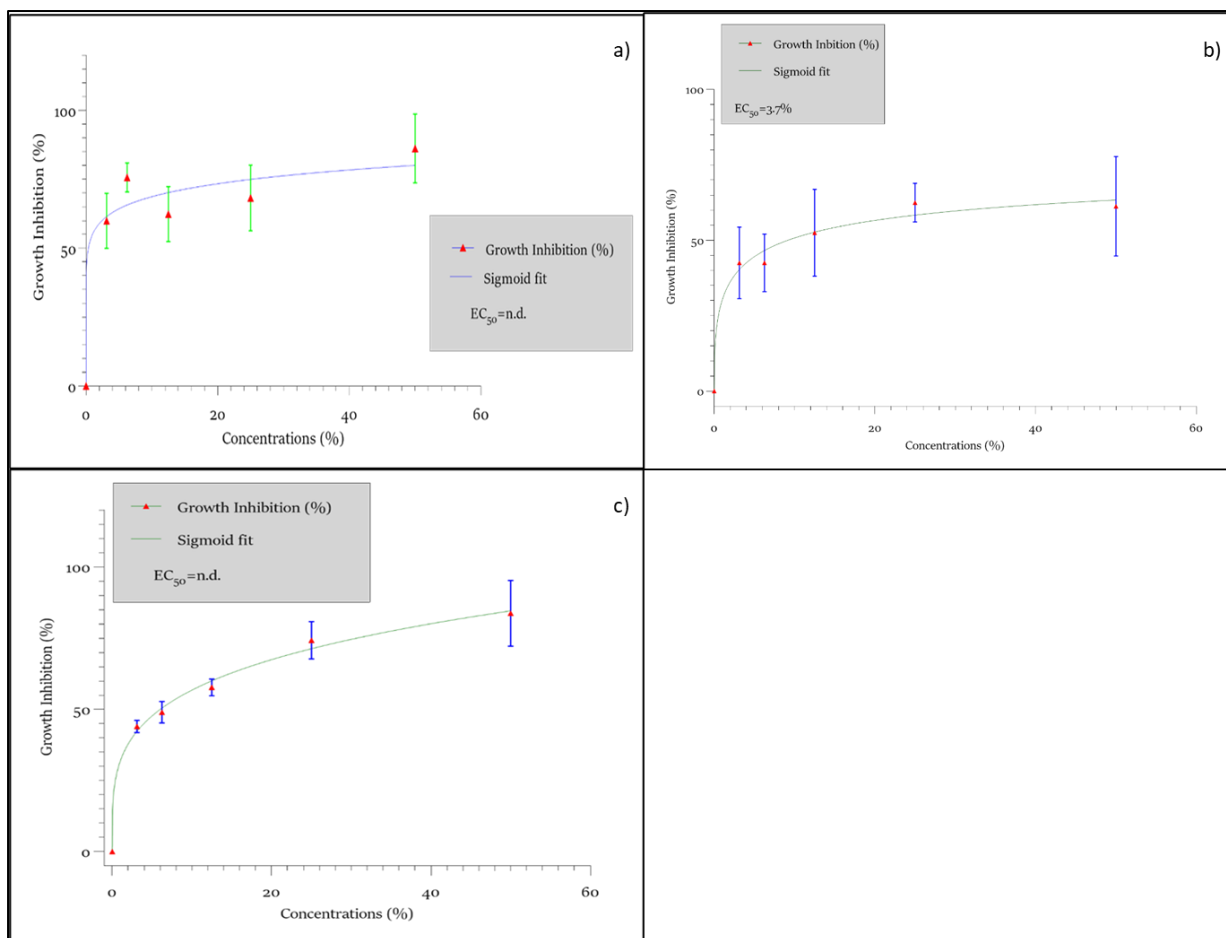


Figure 7.3: Growth inhibition of algae exposed to CNT brick leachates at a) neutral, b) acidic, and c) basic medium

7.2.4.2 *Daphnia magna*

The immobilized neonates (infant daphnia) exposed to pristine brick leachates under varied conditions are presented in Figure 7.4. A very low 72h E₅₀ of 0.0007614% was found for the neutral leachate, at an acidic pH the E₅₀ was 3.95% and no data was determined for the basic leachate. In neutral medium, Cr (0.2 mg/l), Cu (0.9 mg/l), Cd (0.01) were higher than the E₅₀ of *D. magna* recorded in literature, i.e., 0.13 mg/l, 0.013 mg/l and 0.0036 mg/l for the heavy metals respectively [43]. In acidic conditions, As (6.2 mg/l), Cu (0.8 mg/l), V (3.8 mg/l), Cd (2.3 mg/l), Zn (8.0 mg/l) were higher than the EC₅₀ of 2.4 mg/l, 0.013 mg/l, 1.2 mg/l, 0.72 mg/l for

the heavy metals respectively. Lastly, in basic medium only Cd (0.008 mg/l) was above the EC₅₀ of 0.0036 mg/l [43].

The heavy metals leached above the EC₅₀ for *D. magna* in different leachates and were the cause of the high toxicity and immobilization of the neonates. The neutral leachate had a lower EC₅₀ compared to the acidic leachate even though the acidic leachate had more heavy metals leached at high concentrations. However, the total immobilization after 72 h exposure was 100% for the acidic leachate compared to the 45% immobilization at the highest leachate concentration of 50%. The basic leachate immobilised over 40% neonates at the highest concentration. An increase in concentration of the neutral leachate did not show a significant effect on the neonates. While a different effect was observed for the acidic and basic leachates. An increase in the leachate concentration increased the number of the immobilised neonates.

In a literature study, the E₅₀ of CFA leachate to *D. magna* was found to be 30.8% after 48 h exposure to an unadjusted pH solution [44]. The toxicity was lower due to the shorter exposure time and the CFA leachate had lower levels of heavy metals compared to this study. The high toxicity of the leachates to *D. magna* compared to the microalgae (Figures 7.3 and 7.4) was due to the high sensitivity of *D. magna* to unfavourable conditions. Similar results were found that *D. magna* using the diverse test organisms (bacteria, microalga, crustacean, and rotifer), and the method was found to be the most sensitive test for the evaluation of the ecotoxicity of CFA leachates [44].

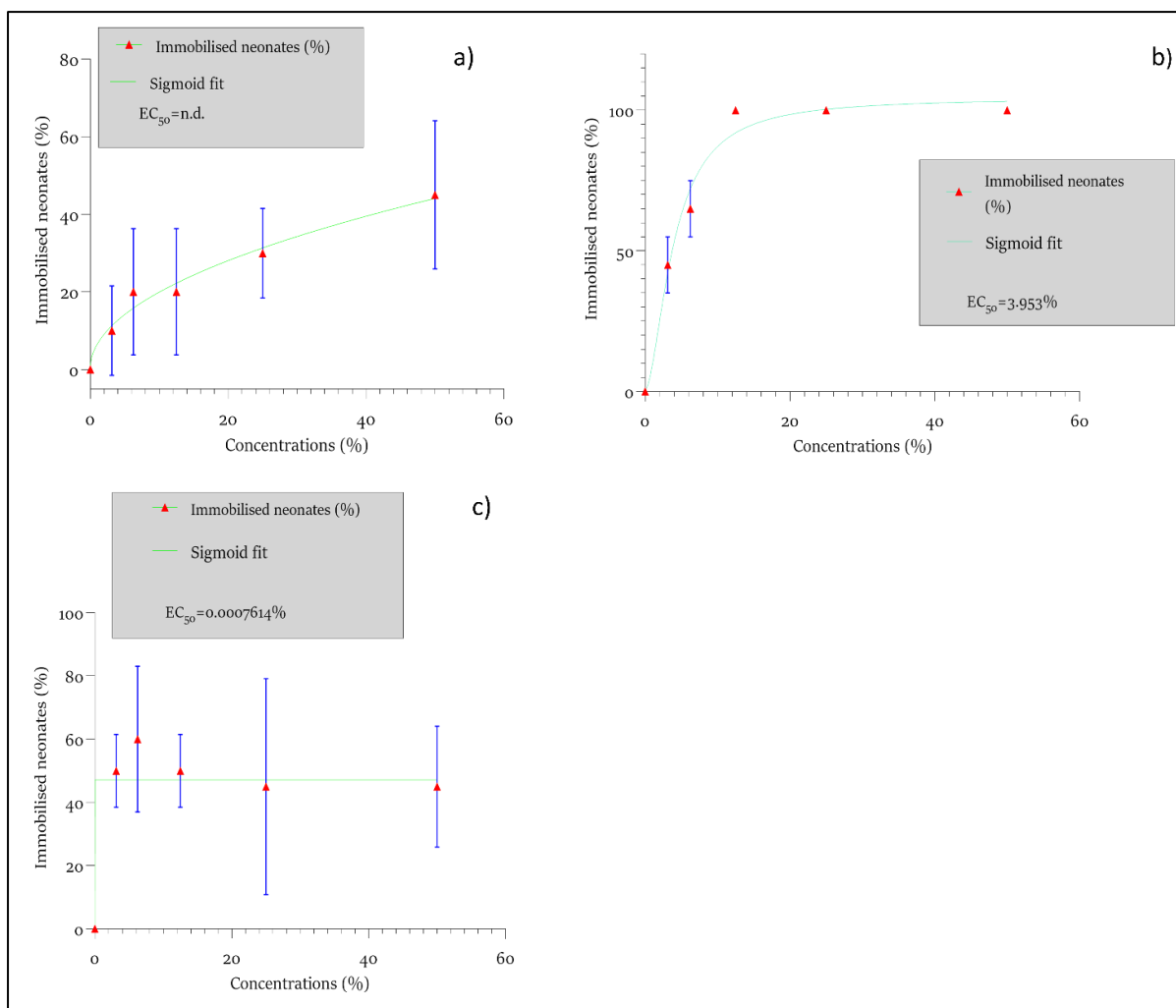


Figure 7. 4: Immobilised neonates exposed to pristine brick leachates in a) neutral, b) acidic, and c) basic medium

Figure 7.5 shows the immobilised neonates exposed to CNT brick leachates at different pH levels. The EC₅₀ was determined for the acid leachate and found to be 3.215%. The leachates were toxic to the neonates. In neutral conditions, Cr (0.3 mg/l), Cu (0.8 mg/l), Cd (0.07) and Zn (1.1 mg/l) were above the reported EC₅₀ of 0.13 mg/l, 0.013 mg/l, 0.0036 mg/l and 0.72 mg/l for the heavy metals respectively. In acidic medium, As (2.3 mg/l), Co (1.1 mg/l), Cu (1.7 mg/l), V (2.8 mg/l), Cd (0.02 mg/l) and Zn (3.5 mg/l) were higher than the EC₅₀ of 2.4 mg/l, 0.71 mg/l, 0.13 mg/l, 0.013 mg/l, 0.0036 mg/l and 0.72 mg/l for the heavy metals respectively. Lastly, in basic medium Cr (0.3 mg/l) and Cu (1.6 mg/l) were higher than the EC₅₀ for *D. magna* [43].

At the highest leachate concentration, the immobilised neonates were 85%, 100% and 45% for the neutral, acidic and basic mediums respectively. The toxicity of the neutral CNT leachate to the neonates was increased compared the pristine leachate (Figure 7.3). This was due to the higher concentration of leached heavy metals. Meanwhile, the toxicity of the leachates to the neonates in acidic and basic medium was similar in pristine and CNT brick leachates. This showed that the heavy metals present in the leachates had more effect on the toxicity of the leachates to the neonates compared to the CNTs.

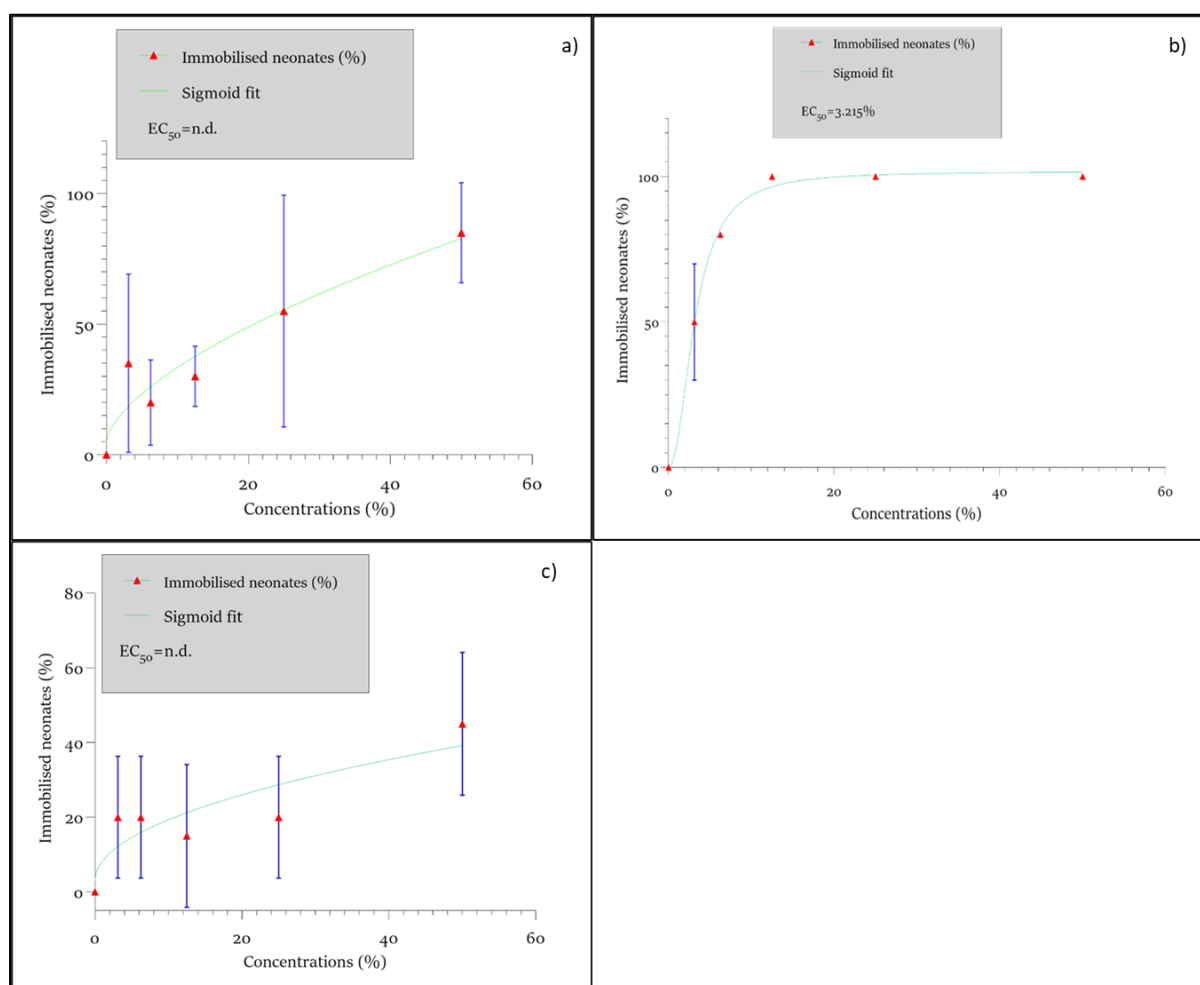


Figure 7.5: Immobilised neonates exposed to CNT brick leachates in a) neutral, b) acidic, and c) basic medium

7.2.5 CNT leaching

Figure 7.6 shows the TEM and EDS results of CNT brick leachates under neutral, acidic and basic medium respectively. The neutral and acid samples did not leach CNTs. However, in

acidic medium, more elements (from CFA) were leached out. This was also observed from the ICP results (Table 7.4) with higher concentrations of heavy metals leached in acidic conditions. This was attributed to a greater affinity of metals leaching with decreased pH levels. The CNTs were leached in a basic medium, as shown by the TEM image and EDS results.

The toxicity of CNTs is still unclear. However, the major concern with CNT leaching is the potential release of metals such as iron (Fe), nickel (Ni) or cobalt (Co) used as catalysts or supports in their synthesis [45]. These are observed as impurities at different levels in CNTs. It has been shown that even purified CNTs can still contain traces of metals that can be potentially released into the environment from the leached CNTs. Furthermore, the functionalization of CNTs for improved surface chemistry can have an effect on their interaction with other elements or compounds within the medium into which they are leached. Wang et al., [46] studied the effect of CNTs on Cd toxicity to *D. magna*. It was found that the presence of CNTs enhanced the toxicity of Cd to *D. magna* due to the greater adsorption of Cd to the hydroxyl functionalized CNTs. Meanwhile, the toxicity of pristine CNTs was only due to the presence of metal catalyst impurities [46].

Interestingly, in the CNT leached sample (Figure 7.6), the Fe used as a catalyst was not detected. The concentration might have been too low for detection or the Fe was not removed from the CNT. In this study, the potential release of CNTs in the application product (bricks) was reduced by the use of small quantities of CNTs (0.05 wt.% used) and their immobilization within the polymer matrix. Interestingly, these tests were conducted on crushed bricks which exposed the CNTs and metals to leaching.

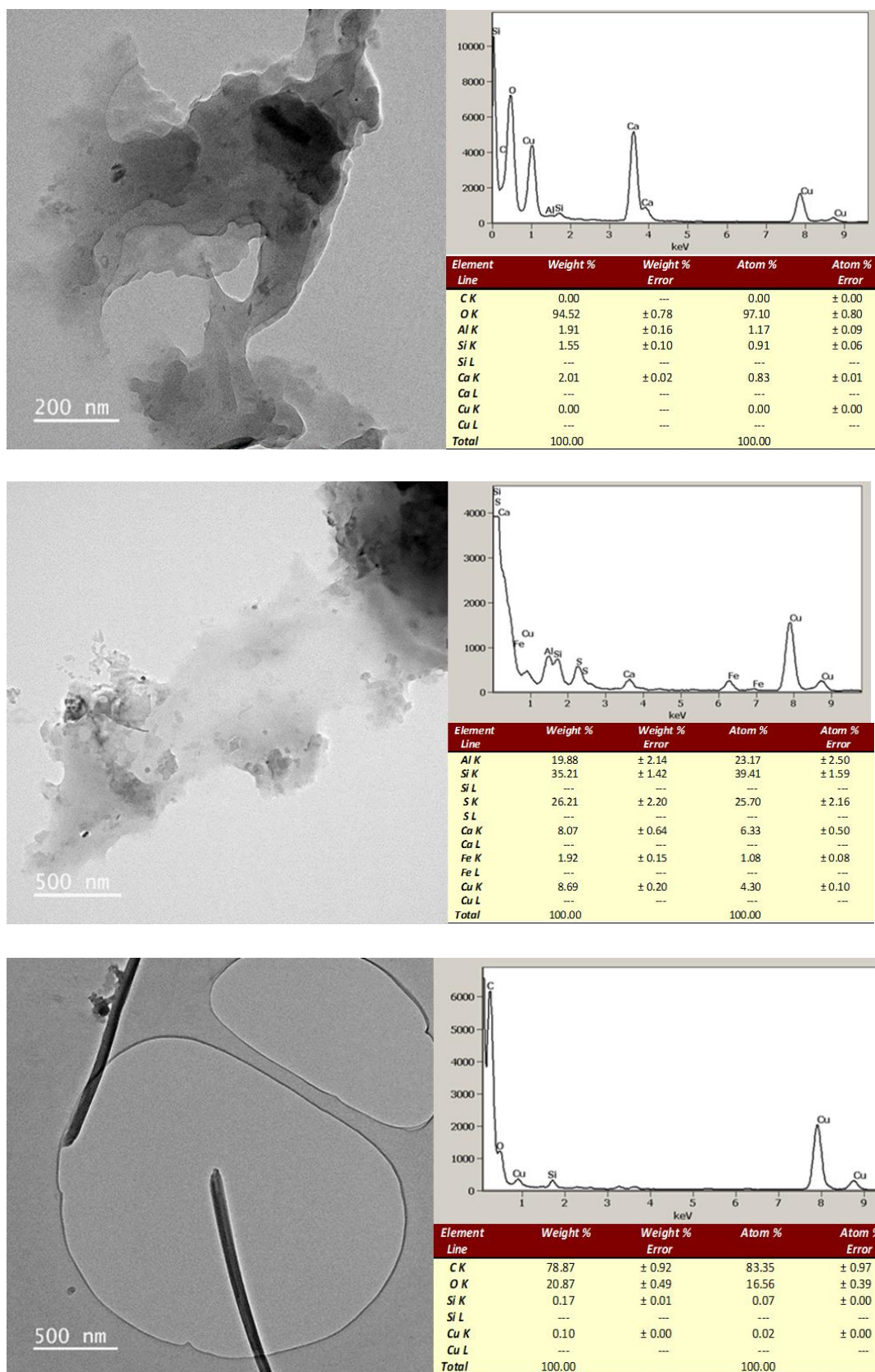


Figure 7.6: TEM image and EDS of CNT brick a) neutral, b) acidic, and basic leachate

7.3 Conclusion

The environmental and economic sustainability of the brick manufacturing industry is important. As such, interventions to make the industry more sustainable, such as using alternative raw materials (i.e. waste) and renewable energy sources are constantly being investigated and adopted. The brick industry is a very competitive one because a small cost saving per brick makes a significant difference in the overall construction process and costing.

The use of waste materials in building is reliant upon a number of aspects, including affordability, lower disposal costs, preservation of resources, market demand, legal requirements, durability, and technological improvements. Waste materials can provide financial advantages and support sustainable construction practices by reducing pollution, preserving resources, and lessening environmental effects when properly assessed and integrated into construction practices. It is imperative to carry out comprehensive investigations, evaluations, and assessments to ascertain the appropriateness and efficacy of waste materials in construction applications.

In this study, CFA and CNTs were tested for their environmental and economic sustainability in building bricks. An extreme case was used where powders were measured. The effect from non-powder materials will be much less. The CFA showed high leachability of heavy metals especially in acidic conditions, which was a concern. The leachates were toxic to the test organisms (*D. magna* and *R. subcapitata*), especially to *D. magna* showing 100% immobilization of the neonates after 72 h exposure to the acidic leachate. Thus, the CFA needs to be treated prior to application to remove the toxic heavy metals to ensure safe utilization. The CNTs were shown to have leached only in basic conditions and their effect on the test organism was inconclusive. As such, dedicated tests still need to be conducted only with CNTs without the CFA. Furthermore, the cost analysis showed a resource saving on the utilization of CFA and waste plastics in the bricks. This reduced the dependency on the non-renewable resources and the overall cost of raw materials. The main cost was from the CNTs which can be reduced by their percentage loading, guided by the required properties in application. The waste-derived CNT bricks can be competitive with the conventional bricks based on cost, properties and environmental impact. However, their ecotoxicology must be thoroughly understood for their safe application.

7.4 References

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CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

8.1.1 Synthesis of carbon nanotubes

The optimization of CNT synthesis was crucial to ensure that they are scalable, affordable and easily adoptable for large-scale industrial application such as the building sector. In this study, the CNTs were produced using a CCVD method that was facile and could be continuous for high volume production. The effect of temperature was investigated and defected CNTs with impurities were formed at a lower temperature of 750 °C. This was due to the low rate of decomposition of hydrocarbons hindering the growth of highly crystalline CNTs. At higher temperatures 850 °C more crystalline CNTs were formed with minimal impurities. Furthermore, the effect of the catalyst-carbon source injection rate was studied and found that an increase in the injection rate resulted in decreased crystallinity due to insufficient time for the reactant to form crystalline CNTs in the furnace. Lastly, the effect of nitrogen (N₂) carrier gas resulted in a decrease in the diameter of the CNTs at higher N₂ flow rate and a reduction in the crystallinity of the CNTs.

The optimization reactions allowed CNTs of high purity and yield to be obtained for application in building bricks. The CNTs were highly crystalline which resulted in high mechanical strength and thermal stability for their application. The CNTs were synthesized at a shorter reaction time using minimal reactants in order to reduce their carbon footprint for improve environmental sustainability.

8.1.2 Application of CNTs in bricks

Coal fly ash (CFA) was the chosen aggregate over coal bottom ash (CBA), due to its higher availability, lower content of heavy metals and spherical particles which have been shown to aid better filler effect, thus improving the overall mechanical strength. The effect of CFA to low density polyethylene (LDPE) ratio was studied and the optimum ratio was found to be

85:15 respectively. The ratio ensured good workability and compaction of the bricks for high mechanical strength. The curing time (3-28 days) showed an improvement in the strength of the bricks. However, beyond 14 days there was minimal improvement in strength because the settling rate of polymer composites is high. The compressive strength was found to be 10.9 MPa after 28 days.

The effect of functionalized CNTs was studied on the CFA bricks. The functionalization of CNTs was to improve the surface chemistry for enhanced interfacial interaction within the composite matrix for homogeneity and improved properties. The CNT loading was between 0-0.1 wt.%, and an increase in CNT loading until 0.05 wt.% showed an improvement in the overall properties (split tensile strength, compressive strength, microstructure and water absorption) of the bricks. However, as the CNT loading was increased to 0.1 wt.% the CNT agglomerated in the composite which resulted in the formation of weaker spots that formed cracks upon load application. The optimum CNT loading was 0.05 wt.% which improved the microstructure of the bricks by filling the voids and providing a bridging effect within the composite as mechanisms of reinforcement. Furthermore, the water absorption was reduced, as a result of the formation of more densified bricks which indicated reduced porosity. The bricks exceeded the required standard of 4 MPa and 1.2 MPa for the compressive and tensile strength respectively for all the bricks. As such, the bricks showed great applicability in the building and construction industry.

8.1.3 Durability of the CNT-bricks

The CNT bricks were tested for their durability using chloride conductivity (CCI), water sorptivity (WSI) and oxygen permeability (OPI) indexes. Again, they were tested for chemical attack, thermal stability and efflorescence. The tests were performed with the CNT loaded bricks and the control bricks (0 wt.% CNT loading). The CNT bricks showed improvements with the durability indexes as well as the thermal stability. This was due to the improved microstructure of the brick which densified their structures and reduced their susceptibility to losses in structural integrity. The control and 0.01 wt.% bricks failed the OPI tests due to their low density and high porosity. Furthermore, only the 0.05 wt.% bricks were classified as “good” for the WSI test while the others were classified as “poor”. It is worth noting that the

indexes are mainly used for concrete which requires very low to no water absorption while, the bricks require a level of water absorption to bind with the mortar during building. All the bricks were within the good category for the CCI, but the CNT-reinforced bricks performed better. The CNTs in the bricks aided thermal stability properties and the bricks maintained their structural integrity beyond 220 °C where the control bricks failed. The acid and basic chemical resistance of the bricks improved upon the inclusion of the CNTs because of the densified microstructures. Lastly, the bricks showed minimal efflorescence which had no effect on the structural integrity or durability of the bricks.

8.1.4 Environmental and economic sustainability of CNT-bricks

The bricks were tested for environmental and economic sustainability using the control and optimum 0.05 wt.% CNT bricks. The bricks developed in this study were compared with the conventional bricks such as clay, concrete and geopolymer bricks. A reduced environmental impact due to the application of waste (CFA and plastic) was observed. The application of waste contributed towards resource conservation, reduced carbon footprint, reduced disposal costs and overall production costs. The developed bricks did not require the high energy conventionally required for drying and firing especially clay brick and also no water or cement was used during production. Thus, the total resource saving was 336 kg per 112 bricks developed. The cost per brick for the 0.05 wt.% CNTs brick was determined to be \$0.091 when considering only the raw materials. Which was lower than the cement bricks (\$0.23) but slightly higher than the clay bricks (\$0.089) which have their major cost coming from energy consumption which was not calculated. The cost per brick of the CNT reinforced bricks can be reduced by reducing the loading percentage to fit the desired properties.

The ecotoxicology studies were performed on powdered samples of control and CNT bricks. The samples were leached in neutral, acidic and basic conditions and tested on a microalga (*R. subcapitata*) and aquatic organism (*D. magna*). The leachates released some heavy metals (from CFA) beyond the leaching concentration threshold recommended by the SANBS. As such they were toxic to *R. subcapitata* and *D. magna* and led to growth inhibition and immobilization respectively. The most potent leachate was the acidic one because the heavy

metals have high affinity of leaching in low pH levels. The effect of CNTs on the test species was inconclusive and the CNTs were only leached in basic conditions.

Overall, the waste derived bricks have a great potential of being used as building bricks. They showed competitiveness in reduced environmental impact, resource conservation, reduced cost and superior properties. However, their ecotoxicology must be thoroughly understood for safe application.

8.2 Recommendations

- The CNTs applied in the waste derived bricks can be synthesized using green precursors for a more environmentally sustainable product.
- More durability test standards need to be developed especially for waste derived bricks for their long- term application. This will increase their acceptance by consumers and fast-track the efforts towards greener building materials.
- The cost analysis needs to be thoroughly conducted as it is the major driver of a product's sale. This is especially in the building and construction industry where a minor save has a great impact in the overall cost since it's a high-volume industry.
- The CFA used must be thoroughly tested and the levels of leachable heavy metals understood prior to their application. If needs be the CFA must be treated prior to reduce the levels of heavy metals to ensure their safe application and end-of-life cycle.
- Ecotoxicology studies need to be also performed with solid brick leachates and not only the powder leachates. This will give a true reflection of the leachability of the heavy metals in the application product (bricks). Which might be lower due to being bond composite matrix.
- Ecotoxicology test with only CNTs need to be performed to understand their impact rather than in a matrix with high levels of heavy metals which may overshadow their effect.