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Development of Multiscale Cementitious Composite using Micro Crystalline Cellulose and Multi-Wall Carbon Nanotubes as reinforcement

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Dissertation of Master in
Sustainable Built Environment

Supervisor:
Professor Raúl Fangueiro

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ABSTRACT:

Nanomaterials are attracting substantial interest from the construction industry in the last decades. Due to their remarkable mechanical properties, various nanomaterials are now being investigated as effective reinforcements of cementitious composites. Many types of nano and micro materials are under study to improve the cementitious matrices. However, the commercialization of such new composites is still infeasible due to the challenges that face those materials, especially dispersion difficulties.

This thesis goal was to improve the mechanical properties of cementitious materials using both Multiwalled carbon nanotubes (MWCNTs) and Microcrystalline cellulose (MCC) as a multiscale reinforcement system. The crucial challenge in such procedures is to achieve good dispersion. Thus, unconventional dispersion technique was utilized by combining physical (mechanical stirring and ultrasonication) and Chemical (using Pluronic F-127 and CTAB as surfactants) techniques of dispersion. Also, the optimal surfactant concentrations with respect to MCC and MWCNT concentration were experimentally explored.

The results demonstrated that the incorporation of MWCNTs and MCCs positively enhanced the microstructure and the mechanical properties of the cementitious composite. Among the best results, we achieved 26% and 13% improvement in the compressive strength compared to the plain mortar using 0.2% MCC and 0.1% MWCNT with an optimum concentration of CTAB. While we reached 13% improvement in the compressive strength and 14% in the flexural strength using 0.2%MCC and 0.1%MWCNT with Pluronic F-127 as a dispersion agent. This research investigates the probable mechanical improvement of MCC-MWCNT multiscale composites.

Keywords: Micro Crystalline Cellulose; Carbon Nanotubes; Dispersion; Mechanical Properties; Multi-Scale Cementitious Composites.

RESUMO:

Os nanomateriais têm atraído atenção substancial da indústria da construção nas últimas décadas. Devido às suas excecionais propriedades mecânicas, vários nanomateriais estão atualmente a ser investigados como reforços efetivos de compositos cimentícios. Muitos nano e micro materiais estão sob investigação para reforço de matrizes cimentícias. No entanto, a comercialização desses compositos inovadores em larga escala não é ainda possível, devido aos diversos desafios associados, por exemplo, à sua dispersão.

O objetivo deste trabalho foi melhorar o desempenho mecânico de materiais cimentícios utilizando nanotubos de carbon e cellulose microcritalina, como sistema de reforço à multiescala. O desafio mais importante, neste caso, é conseguir uma boa dispersão. Assim, utilizou-se técnicas de dispersão não-convencionais combinando métodos físicos (agitação mecânica e ultrasons) e químicos (usando Pluronic F-127 e CTAB como dispersantes). Também as concentrações de dispersantes em relação às dos MCC e MWCNT forma experimentalmente estudadas.

Os resultados demonstram que a incorporação de MWCNT e MCC melhoram a microestrutura e as propriedades mecânicas dos compósitos cimentícios. De entre os melhores resultados, conseguiram-se melhorias de 26% e 13% na resistência à compressão, relativamente à argamassa de referência, adicionando 0,2% de MCC e 0,1% de MWCNT, com uma concentração ótima de CTAB. Da mesma forma, conseguiram-se aumentos de 13% de resistência à compressão e de 14% na resistência à flexão, utilizando 0.2% de MCC e 0.1% de MWCNT com Pluronic F-127.

Palavras chave: Celulose microcristalina; Nanotubos de carbono; Dispersão; Propriedades mecânicas; Compostos de cimento multi-escala.

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List of Acronyms

AG	Arabic Gum
CMC	Critical Micelle Concentration
CNT	Carbon Nanotube
C-S-H	Calcium Silicate Hydrate
CVD	Chemical Vapor Deposition
CTAB	Cetyltrimethylammonium Bromide
DWCNT	Double-Walled Carbon Nanotube
MCC	Micro Crystalline Cellulose
MNMs	Manufactured Nanomaterials
MWCNT	Multi Walled Carbon Nanotube
NCC	Nano Crystalline Cellulose
NaDDBS	Sodium 4-Dodecylbenzenesulfonate
NaDC	Sodium Deoxycholate
SDS	Sodium Dodecane-1-Sulfonate
SEM	Scanning Electron Microscope
SWCNT	Single Wall Carbon Nanotube
TBP	Tributyl Phosphate
UV-Vis	Ultra Violet- Visible
VCNF	Vapor-grown carbon nanofiber

Chapter 1

Introduction

1.1 Framework

Construction materials have differed along the history, yet concrete has been the base of construction growth in all over the world in the last two centuries. It is now the most used construction material worldwide mainly due to its low cost and high compressive strength [1]. The research and study on improving the properties of this material run extensively and continuously. New forms of reinforcement, new mixtures, and new building methodologies are parts of the development process of concrete thermal, mechanical or even electrochemical properties.

Using the new techniques, nanotechnology revalorized many industries. The ability to design the material upon a specific interest and from the smallest scale and level opened a promising future. The concrete industry uses nanotechnology to reproduce materials with nanoscale improved characteristics. As there is a raising interest of the optimization of traditional concrete properties and other cementitious materials, which is enforcing the research on developing new types of materials [2]. Nanomaterials technology is highly auspicious and important field of research as they have noteworthy characteristics and useful applications, with a stronger, smarter, and more durable behavior [3] [4]. Nanotubes and other nanomaterials have enhanced the concrete properties evidently when used with polymeric matrices [5]

The integration of nanomaterials in concrete has been increasingly vital to the concrete industry. Carbon nanotubes (CNTs), invented by Iijima in 1991, consisting of carbon particles with a tubular morphology and nanometer diameter. They have a high theoretical strength, 100 times more than regular steel and an elastic strain capacity 60 times more than steel. They have been used in a variety of applications starting from electrical to chemical and multi-functional composites. They hold a high interaction potential, which allows CNT to form bundled structures. Moreover, they showed great improvements in the mechanical, electrical, and electromagnetic behavior of composites and especially the polymer based ones [6][7][8].

In a parallel field, natural fibers have been used in cement-based materials since a long time, due to their useful properties to cement based materials. Microcrystalline celluloses (MCCs) are the type of natural fibers, which callouses chains are disposed of in repetitive arrays to produce crystals. MCC materials demonstrated a hopeful development for the cement-based materials, as they possess hydrophilic character and water retention capability, which are especially interesting to the cement [9].

1.2 Objectives

The main object of this thesis is to study the performance of cementitious composite with the combination of microcrystalline cellulose (MCC) and multi-walled carbon nanotubes as reinforcements (MWCNT) through a novel dispersion method. The development and characterization of CNT reinforced cementitious composites and MCC reinforced cementitious composites have been investigated in this work. The multi-scale incorporation (Micro-Nano) is an original approach, thus and considering both materials properties, it is expected to develop a high-performance cementitious composite.

For the sake of acquiring the best analysis of the composite performance, different compositions were made with different percentages of carbon nanotubes and microcrystalline cellulose, and different combinations of surfactants.

1.3 Methodology

The methodology for conducting this research was developed through two phases.

The first one includes a state of the art review to analyze the knowledge provided by other authors one both materials, MWCNT and MCC, and on the attempts to have multi-scale incorporation of other materials as well as dispersion methods on cement based materials.

In the second phase, the work was conducted through the experimental laboratory work, which consisted of two cycles: the first cycle comprised the preparation and development of cementitious matrix composites with MWCNT and MCC, explaining the dispersion process and presenting the various compositions used, as well as presenting the results analysis of the compression and tensile behavior of the cementitious composite. The second cycle was completed to investigate the enhancement and the changes happened, based on the configuration of the composites by correcting the percentages and involving other surfactants.

1.4 Dissertation Plan

The dissertation is divided into five main chapters including:

- Chapter 1 - Introduction.

The first chapter introduces the framework of the dissertation; also, it summarizes its objectives, as well as selected methodology and the outline.

- Chapter 2 – Literature review.

The second chapter aims to present a comprehensive review of the various research published on the different themes developed. The previous work conducted by other researchers is critically analyzed to provide a better understanding of the concepts as well as to address future difficulties and proposed solutions. Due to the novelty of the combination MCC and CNT, the review discusses each theme aside.

The main covered themes in the literature review are the composite materials, cementitious matrix materials, carbon nanomaterials, MCC reinforced cementitious composites, CNT-reinforced cementitious composites. The main characteristics of the former materials are discussed as well as forms of production, different applications, dispersion techniques and their mechanical properties.

- Chapter 3 - Materials and Methods: Dispersion of Carbon Nanotubes and Microcrystalline Cellulose in Aqueous Suspension

The third chapter discusses the dispersion of MWCNT and MCC in an aqueous medium using first Cetyltrimethylammonium bromide (CTAB) and Pluronic F-127. It discusses also characteristics of prepared suspensions such as homogeneity and agglomeration. In addition, it discusses the conclusions of the optimal surfactant concentrations for achieving homogeneous and stable MWCNT and MCC suspensions.

- Chapter 4 - Development of Carbon Nanotube and Microcrystalline Cellulose Reinforced Cementitious Composites

The fourth chapter discusses the preparation of the multiscale composites with attention to the effects of different combinations of the composite using different surfactants. It also addresses the mechanical properties of the cementitious composites reinforced with MWCNT and MCC.

The laboratory work is analyzed as well as the two rounds of the work and the performed tests to acquire the results. The conditions and process to acquire the best combination of the cementitious composite reinforced with MWCNT and MCC are discussed in details.

- Chapter 5 - Conclusion and Future Work.

The last chapter presents the summary conclusion of the dissertation, presenting the obtained optimum results and proposing the future scope of work to complement the present dissertation.

Chapter 2

Literature Review

The second chapter aims to present a comprehensive review of the various published research on the different developed themes. The previous work conducted by other researchers is critically analyzed to provide a better understanding of the concepts as well as to address future difficulties and proposed solutions.

The main covered themes in the literature review include composite materials, cementitious matrix materials, carbon nanomaterials, MCC reinforced cementitious composites, and MWCNT-reinforced cementitious composites. The main characteristics of the former materials are discussed, as well as forms of production, different applications, dispersion techniques and their different properties.

2.1 Composite Materials

A composite material is a material that has improved characteristics as a result of the combination of two or more individual components combination. Nature has many examples: wood is a combination of cellulose fibers in a lignin matrix. One of the most famous industrial composite materials is concrete [10]. Reinforced concrete, for example, is the more developed composite, as it is a combination of concrete and steel or other reinforcing agents. The resulted properties of the reinforced concrete gather the high compressive strength and the high tensile strength of the steel to form an improved material.

The new concept of composite presently is a material made artificially from two or more different materials that are chemically different and separated by a distinct interface. Thus, the current composite materials used in engineering can be described in two components at least, the matrix which is a continuous and surrounds the second component which is the reinforcement dispersed phase. The main aim for the development of composite materials is to enhance certain properties such as mechanical, thermal, electrical, etc. [11].

2.2 Cementitious Matrix

Concrete is the second most human used substance in the world after water. It is, at the most basic level, a combination of water, aggregates, and more importantly the cement based materials, as bonding agents. When this composite is placed and cured, it hardens to shape a rigid mass called concrete. The hardening process, called hydration, is a result of chemical reactions between water and cement. This process starts after the molding and continues for a long time allowing the concrete to gain strength with age, the chemical changes starts in the first three days to reach good numbers at its 28 days and continue slowly with time.

The properties of the concrete depend on the properties of its components, proportions of the mixture, the compaction method, and the other controlling factors. The basic components are the ordinary Portland cement, the most used cementing ingredient and the principal binding agent, aggregates (normally naturally occurring such as sand, crushed stone and gravel and it can be artificial as the synthetic and recycled materials), water, fillers (such as sand), admixtures (chemical materials which added to improve specific characteristics or accelerate the process), and other supplementary cementing materials. Typical constituents of Portland cement are: tricalcium silicate $(CaO)_3 \cdot SiO_2$ (20 - 65%), dicalcium silicate $(CaO)_2 \cdot SiO_2$ (10 - 55%), tricalcium aluminate $(CaO)_3 \cdot Al_2O_3$ (0 - 15%) and tetra calcium alumino ferrate $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$ (5 - 15%) and sometimes Gypsum $CaSO_4 \cdot {}_2 H_2$ (2–10%). These materials react with water forming a mineral glue (calcium silicate hydrate), calcium hydroxide, ettringite, mono sulfate, un-hydrated particles, and air voids. The process of hardening takes time and needs to be implemented under certain conditions of moisture and temperature [12][13].

Concrete presents many high properties, yet it has a high sensitivity to crack formation due to the shrinkage happening when the concrete starts hardening and drying. Cementitious materials are characterized by quasi-brittle behavior. The cracking begins with isolated nano-cracks, which then conjoin to form microcracks and in turn macrocracks. For that, the cementitious matrix should be combined usually with reinforcement, widely steel, to bear the tensile loads.

All these characteristic, of the cementitious matrix, cement paste, is due to the reaction of water and cement mainly, in the hydration process. The reinforcement of the cement paste has been intensively studied and improved, starting from wood and straw to steel, and the research studies on fibers and nanomaterials are increasing. The cracks threat the durability and the strength of the concrete structures as liquids and gasses can enter the matrix through the cracks and cause severe damages. Even in reinforced concrete, the cracks can grow wider and may expose the reinforcement, the exposition could result in corrosion and consequently endanger the concrete structure [14].

The cracking process starts with the lowest nano-cracks, which can grow to form micro and macro cracks with age. Many materials were studied to reinforce and mitigate the cracks. Fibers in all types, glass, carbon, polymeric etc. have been used to enhance the toughness and reduce the cracking, allowing the fibers to bridge the propagating cracks to mitigate the failure of the cementitious matrix [15].

The development of nano and micro technologies led to a development in the studies of construction materials, especially the cement based materials. The micro and nanoscale fiber reinforcements have been highlighted in the research field due to their improvement of the mechanical properties. Nanomaterial-reinforced cementitious composites are relatively recent. Nanomaterials properties allow the reinforcement and control of cracking in nanoscale. The scale of the fibers has an important effect on the cracking process as the microfibers may delay the cracking process, mitigating the growth of the macro-sized cracks, the nano-sized fibers are used to prevent the growth of nano-cracks to microcracks in the matrix [16].

2.3 Nanotechnology in Construction

Nanotechnology was introduced to science more than half century ago, and through the years it made a ground-breaking impact on diverse science, engineering, and industries sectors, including the construction industry. The nanotechnology in basic is the ability to control materials at the level of atoms, molecules, and supramolecular (nanoscale) structures, to create a new enhanced material. The key of these materials is the size of the particles, as the properties of the materials are affected by the scale of nanometers. Those nanoparticles have chemical, physical and electronic properties that could be different from their bulk materials [3].To better understand the name of the field and the different fields of study following categories of scales of materials, see Table 2-1 [17].

Scale (m)	Fields (not inclusive)
10^{-12}	Quantum mechanics
10^{-9}	Molecular Dynamics Nano-mechanics Biophysics
10^{-6}	Elasticity Plasticity Dislocation
10^{-3}	Mechanics of Materials
10^{-0}	Structural analysis

Table 2-1 The different fields of study following categories of scales of materials [17]

Trailing after the high development of nanotechnology applications in biomedical, chemical and electronic industries, the construction industry started searching for a way to advance conventional construction materials using nanomaterials. The many unique characteristics of these materials include but not limited to strength, durability, lightness, heat insulating, antifogging, etc. These properties could give significantly a promising solution for the current construction problems. Despite the relatively high costs of manufactured nanoproducts, their use in construction is highly predicted to grow.

The nanotechnology found and still finding its way in the construction industries, many of the nanomaterials are under research and application. Manufactured nanomaterials (MNMs) such as carbon nanotubes have beneficial applications in construction that need superior structural properties, functional paints, and coatings, or high-resolution sensing/actuating devices. Metal Oxide Nanoparticles such as TiO_2, SiO_2, Al_2O_3 can be used as filling agents to pack pores of the concrete and prevent the development of microspores that can weaken the structure due to the deicers materials attack the concrete through them. Metal nanoparticles such as copper nanoparticles can improve the steel weldability due to the roughness mitigation effect. Magnetic Nickel Nanoparticles can improve the compressive strength by over 15% if added during the formation of the concrete as the magnetic interactions increase the mechanical properties of cement mortars [18].

2.4 **Cellulose and its Structure**

The raising shift in the world demand for renewable sustainable products directed the research toward cellulose. This abundant polymer is a non-petroleum ubiquitous structural polymer that can be found in nature in different properties and forms and has a major load-bearing function in the plants. It has been studied extensively for its many strengths, its elementary nano-fibrillar components, allowed it to have high-strength and high-performance properties with nontoxic nature. This combination of extraordinary mechanical properties (high strength to weight ratio, high tensile strength), renewability (biodegradable), safety and flexibility attracted many industries like cosmetics, pharmaceutical, textile and, recently, construction industry are using it [19]. Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$; it is classified as a carbohydrate. Figure 2-1 presents the structure of cellulose [20] [21].

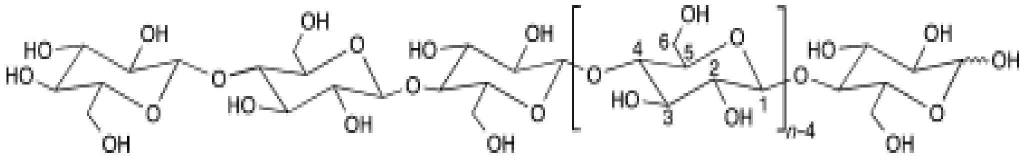

Figure 2-1 Molecular structure of cellulose (n=DP, degree of polymerization) [21]

The cellulose microfibrils can be classified into two types according to the cellulose chains conformations: the cellulose chains are disposed of high organized arrays to form crystalline part, or the chains are arranged in disorder, more flexible confirmation to form an amorphous conformation [9].

Cellulose is a biopolymer, and its nanoparticles can be extracted either mechanically in two different approaches: top down approach and bottom up approach or chemically induced deconstructing strategy. The potential of nano-cellulose for many applications has to be demonstrated, due to its high mechanical properties, transparency, and biodegradability, it is attractive material to the pharmaceutical industry as drug delivery tool, to the textile and paper industry and less fame in the buildings industry. The main challenge of this nanoparticles is the difficulties in dispersing within various matrices. Those nanoparticles tend to self-associate because of the omnipresence of interacting surface hydroxyl groups. While it is a desirable characteristic in some industries as it reflects in high strength and load bearing capacity, yet those inter-particles interactions can limit the protentional mechanical reinforcement in the case of aggregation during the preparation of the nanocomposite. The aggregation potential is decreased when the size of the particle increases [19] [22].

2.5 Microcrystalline Cellulose (MCC)

The bio-nanomaterials led the way for many industries to explore new materials with extraordinary properties. The nanofibers cellulosic materials are known to lower the thermal conductivity, enhance the sound absorption and reduce the plastic shrinkage [23].

Microcrystalline cellulose (MCC) a naturally occurring substance and a cellulosic material were first introduced to the world in 1955 by Battista and Smith [24]. Remarkably, the discovery came from a failed experiment, as the authors were trying to employ a Waring Blender to break up hydrolyzed cellulose to smaller particles in water. Their idea was that the blender sharp blades would sliver off small fragments of the agglomerated microcrystals in the hydrolyzed cellulose, and those fragments would settle out of the water. However, they obtained a stable colloidal suspension, MCC. It was first presented as a commercial product under the name Avicel® in 1962 [25].

The Microcrystalline cellulose (MCC) can be obtained through the top-down approach described as illustrated in Figure 2-2

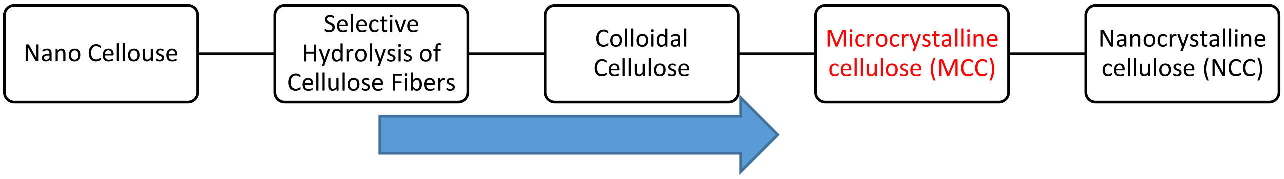

Figure 2-2 Top down approach production for MCC [22]

Microcrystalline cellulose (MCC) has a crystalline structure, it has an aspect ratio around 1, while its dimensions are more than 1μm at least (length, diameter), typical dimensions of dispersed MCC nanofibrils are 20 nm in diameter and around 200 nm in length [26]. MCC is extracted from cellulose by selective hydrolysis of cellulose fibers followed by homogenization. MCC has extraordinary mechanical and physical characteristics: elastic modulus of 120-200 GPa, superior to glass fibers (85GPa) and aramid fibers (65GPa) modules, a tensile strength of 7.5 GPa [9]. MCC applications extend to cover medicine industries, cosmetics, textile, and food; as stabilizers for aqueous suspensions, flow controllers and as reinforcement of final product. Although MCC have been used in the polymeric matrices before, yet the implementation in the construction industry through cement based materials, by incorporating within cementitious matrices is not investigated significantly [27] [9].

MCC microfibrils have high water retention capacity and are highly hydrophilic. The development and elaboration of cementitious materials are highly dependent on the water as a key substance. Thus, the hydrophilic properties and the water retention capability of MCC, are interesting characteristics to study exploring potential applications of MCC in cement material [9].

The cellulose nanocrystals (NCC) have proven to improve flexural strength of the cementitious composite. On the other hand, the MCC particles showed no positive influence on the properties of the cementitious composites in the case of low quality or no dispersion. The agglomeration of MCC is suspected to influence and reduce the reinforcing efficiency and lead to a degradation of the cementitious material mechanical properties.

MCC can be extracted from green plants and vegetables, by hydrolyzing the cellulose chains, in a diluted mineral acid at its boiling temperature. The hydrolysis process works as follow: in the beginning vegetable is selected and shredded, then it is hydrolyzed to convert the insoluble hydroxides, oxides, and sulfates in vegetables into a soluble compound that are removed by a filtration process. The last step, the filter cake is suspended in water and subjected to a spray drying process, yielding the MCC with a size distribution and moisture content following the conditions.

The final product of MCC could take two forms, either a colloidal system when it is equally dispersed and co-processed with a water-soluble polymer or a powdered form of pure particles. Figure 2-3 shows the detailed process in both ways [25].

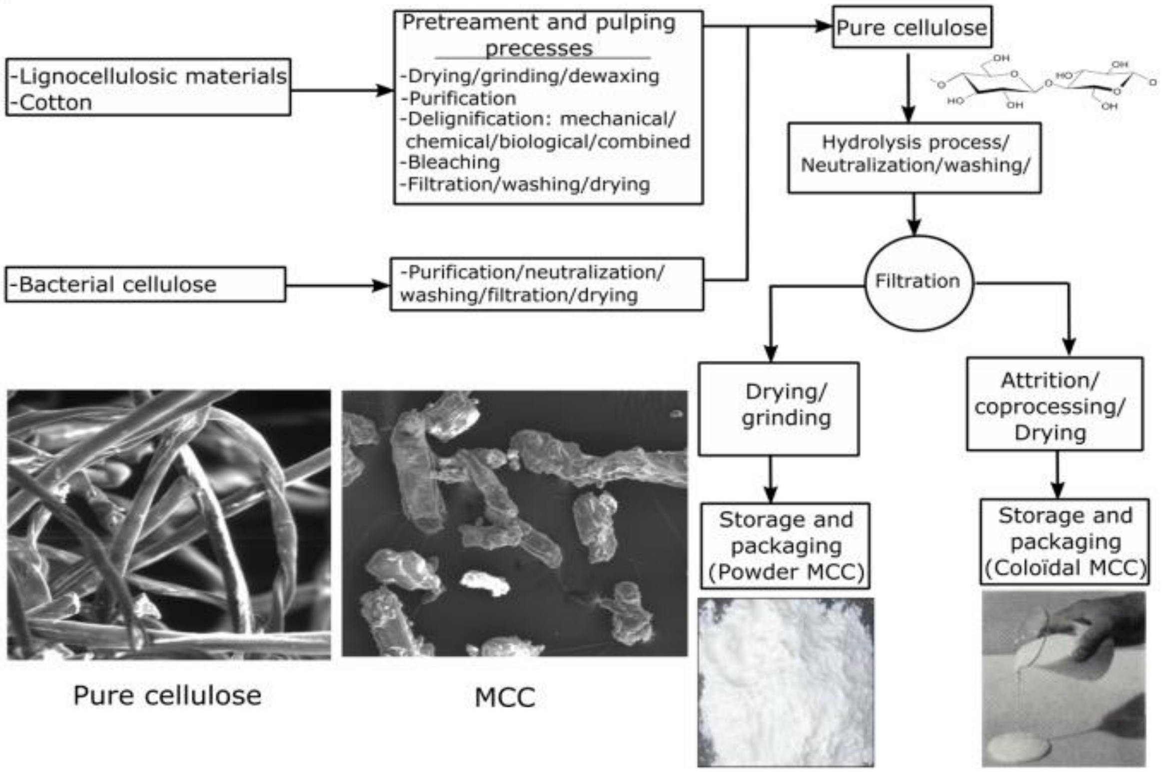

Figure 2-3 Scheme of the common steps needed to produce MCC from cellulose source materials.[25]

2.5.1 Microcrystalline Cellulose (MCC) Sources

The main cellulosic fibers sources of MCC are cotton and wood. Yet, the competition of these fibers among many industries made it a challenge for providers to provide it in the good quality and at the affordable price. Thus, it has been a quite attracting to investigate in other non-woody plants sources such as herbaceous plants, grass, aquatic plants, agricultural crops and the fact that these plants usually comprise less lignin than wood. Therefore, bleaching methods are less chemical and energy demanding [25].

2.5.2 Microcrystalline Cellulose Isolation Techniques

There are many different methods for isolating MCC considering as well that the amount of cellulose in different natural sources can vary depending on the species and age of the plant. The main methods are the following: [25].

1- Acid hydrolysis

Acid hydrolysis is one of the common process used isolating MCC as it requires shorter reaction time than other processes. The process is based on the fact that cellulose microfibrils are composed of crystalline regions and disordered or paracrystalline domains located at the surface and along their main axis. Paracrystalline or amorphous regions cleaved when they contact with acidic solutions, however, the crystalline domains that have a higher resistance to acid attack remain essentially undamaged.

2- Alkali hydrolysis

Alkali hydrolysis is considered the most used technique for de-lignification of lignocellulosic materials. When the material is completely swollen, then hydrogen peroxide is added to the mixing suspension to depolymerize the cellulose thereby reducing viscosity. In the last step, the solution is filtered, neutralized, washed and dried. One of the advantages of this method is that no temperature/high-pressure applications are required and it leads to MCC in an economically efficient manner.

3- Steam explosion

This technique has been extensively studied, as it has many attractive features such as lower environmental impact, fewer hazardous process conditions and higher potential for energy efficiency.

There are two main approaches for obtaining MCC, the first approach has two steps, the first step is extracting the steam-treated lignocellulose to recover a low degree of polymerization cellulose, then this steam-treated lignocellulose is impregnated with strong mineral acid to obtain MCC during the second steam treatment.

In the one-step approach, there is no need for conventional acid hydrolysis as a supplement to steam treatment. MCC here is obtained in one step by a process of introducing a cellulose source material into a pressurized reactor; exposing the cellulosic to a steam explosion under controlled conditions.

4- Extrusion

The main advantage of this technology is the short duration, high flexibility, and nonexistence of effluents, yet it considered high-temperature hydrolysis method

5- Radiation-enzymatic

The last technique has not been investigated widely, as the enzymatic processes to produce MCC are expensive and economically infeasible for applications, and those processes tend to create MCC products having lower crystallinity [28].

2.5.3 Dispersion of Microcrystalline Cellulose (MCC) within Cementitious Matrices

Although, bio-materials are getting high interest from different fields. Yet, the use of MCC within cementitious matrices is relatively not well-known.

MCC has been inspected in few studies as a reinforcement in cementitious materials; in one study [9], MCC was used without any dispersing agent as a composite reinforcement, however, no significant improvements on the mechanical properties of the new composite were reported. A dispersion of MCC was presented. The possible reason is the non-homogeneous and lack of right dispersion method, as a dispersion of MCC is also believed to be highly important with respect to the mechanical properties, as MCC agglomeration can significantly reduce its reinforcing efficiency and leads to defects in cementitious materials.

In another study [27], an attempt to obtain a homogeneous dispersion of MCC within cementitious matrix was presented, with the help of surfactant (Poloxamer 407, trade name Pluronic F-127), a biocompatible surfactant which has been widely used for dispersing CNTs, to produce MCC reinforced cementitious composites. MCC was dispersed successfully using Pluronic F-127. An improved dispersion of cement particles was achieved due to the increase in the bulk density of cement mortar after adding Pluronic F-127 and the dispersed MCC. Enhanced flexural modulus was achieved with the MCC. However, flexural and compressive strengths were highly dependent on various parameters. Maximum improvements in flexural and compressive strengths were 31% and 66%, respectively obtained through addition of 0.5% MCC using Pluronic F-127. Also, the addition of MCC led to better hydration and reduction in pore size of the cementitious matrix [27].

2.5.4 Microcrystalline Cellulose (MCC) Influence on Cement-Based Matrices

The overall effect of MCC is merely depending on the dispersion method and quality. Nonetheless, the tests performed on well dispersed MCC in cementitious matrices showed some aspects of its influence. A mini-slump test was performed for the analysis of flow behavior of cement to determine the workability. MCC reinforced cement matrix has an increase of the yield stress $\tau 0$ by 2.6 times more than the plain cement paste, although that means less workability and more energy consumption during processing of the reinforced mortar. However, in some construction applications, higher τ0 is necessary; for example, MCC reinforcement is suitable for rigid pavements where the fresh paste should retain its shape. On the contrary, MCC reinforcement negatively affected the mechanical properties of the cementitious composite in a normal curing period of 28 days. During accelerated curing conditions, MCC reinforced cementitious composite reached the plain one values [9].

One of the advantages of MCC reinforced cement is its good microstructure, as the available hydroxyl groups of MCC could form hydrogen bonding with the hydration products of cement, thus it remains saturated with water, offering the near growing CSH phase water bound [27].

2.6 Carbon Nanotubes (CNTs)

Carbon nanotubes are hexagonal shaped arrangements of carbon atoms that can be rolled into a tube. Figure 2-4 illustrates the idea of tubes' formation. CNTs are mainly three kinds. Figure 2-5 presents a schematic illustration of the three types.

The first type, multi-walled carbon nanotubes, were discovered by Sumio Iijima in 1991. Multi-walled carbon nanotubes (MWCNT), which are needles like tubes of carbon or a tubular form of carbon, MWCNTs are comprised of multiple layers (concentric tubes) of graphitic shells with shell separation around 0.34 nm and overall high aspect ratio. They attracted special interest for their high physical and mechanical properties [29].

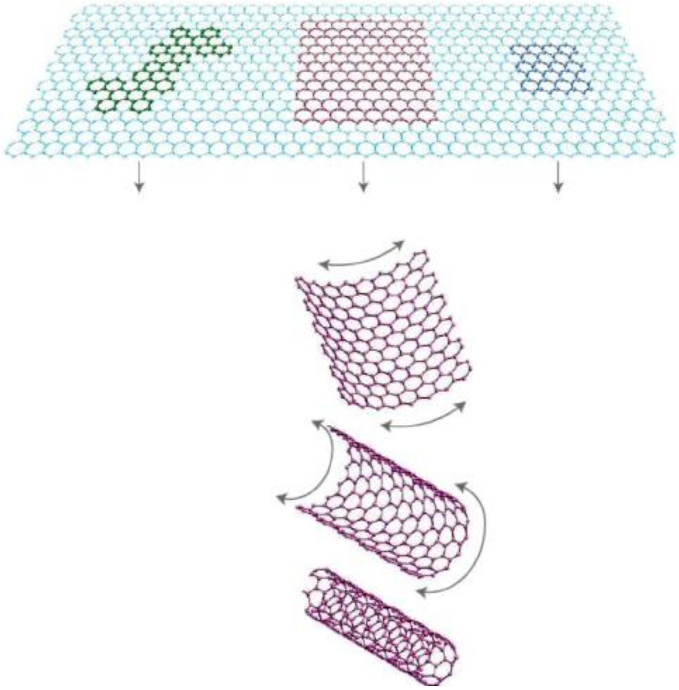

Figure 2-4 Illustration of arrangements of carbon atoms to be rolled into a tube: [28]

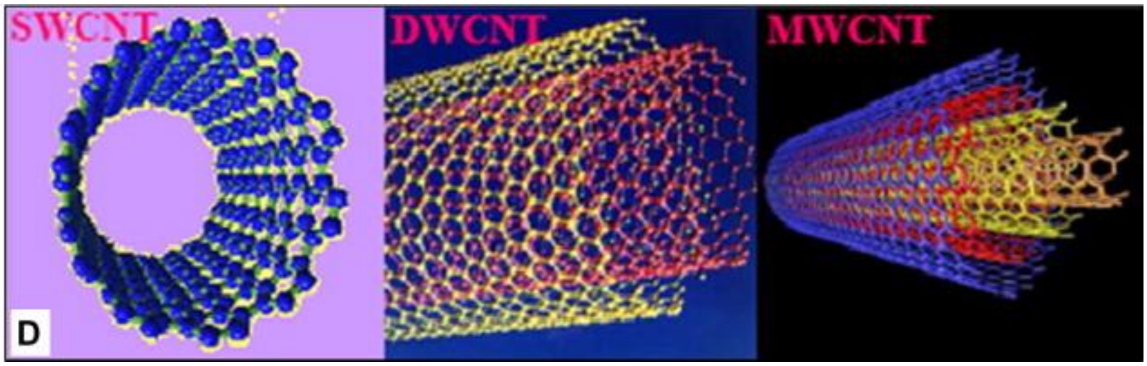

Figure 2-5 Schematic illustration of the three types [28].

The second type of CNT was discovered by Iijima and Bethune in separate research in 1993, single wall carbon nanotubes (SWCNT), which he could isolate to obtain a single sheet of graphite wound as a cylindrical. These (single-walled carbon nanotubes SWCNTs) are generally narrower than the multi-walled tubes, with diameters typically in the range 1–2 nm. SWCNT have 100's times higher strength than commercial high carbon steel with tensile modulus many times higher than steel, and their flexibility is also exceptional as they can stretch over five times their original length with nearly 100% memory and undetectable levels of corresponding structural damage. Thus, SWNTs have interesting physical, morphological and electronic properties and find applications in a variety of areas ranging from biosensors to transistors [29]. The small size of the diameter and the structural instability of SWCNTs introduced difficulties for SWCNT production and analyzations studies, compared to the MWCNT. Figure 2-6 shows the schematic representations and microscopic images of the most common types of CNT, MWCNT, and SWCNT respectively [30].

A less popular, relatively under-explore type of CNTs is Double-Walled Carbon Nanotubes (DWCNTs), which consist of two cover layers of graphite sheets, and they form a special class of nanotubes because their morphology and properties are similar to those of SWNTs but they are more resistant to chemicals showing properties intermediate between SWCNTs and MWCNTs [31][32].

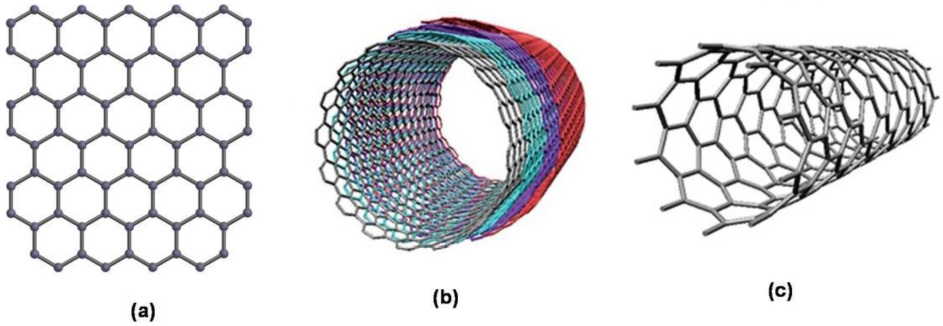

Figure 2-6 Schematic representation of the structure of graphene (a), MWCNT (b) and SWCNT (c) [30]

Overall carbon nanotubes have extraordinary mechanical, electronic, thermal, optical and chemical characteristics such as the high Young's modulus around (1.4 TPa), current density (109 A/cm^2, tensile strength (above 100GPa), enhanced electronic properties, including ballistic, transport, and thermal conductivity (above 3000W/mK), as well as the remarkable flexibility and high breaking elongation (20–30%) [30] [29] . Tables 2-2 and Table 2-3 indicate the properties of CNT compared to other fiber materials.

Fiber Material	Young modulus, E [GPa]	Tensile strength [GPa]	Strain at break [%]	Density [g/cm^3]
Carbon nanotube	1	10-60	10	1.3-2.0
Carbon fiber – PAN	0.2-0.6	1.7-5.0	0.3-2.4	1.7-2.0
Carbon fiber – Pitch	0.40-0.96	2.2-3.3	0.27-0.60	2.0-2.2
High Speed Steels fiber	0.2	4.1	<10	7.8
E or S glass fiber	0.07-0.08	2.4-4.5	4.8	2.5

Table 2-2 properties of CNT compared to other fiber materials [29]

Fiber material	**Electrical resistivity [Ω/m]**	**Max current density [A/m^2]**	**Density [g/cm^3]**
Carbon nanotube alone	10^{-8}	10^{ii}	1.3-2.0
Carbon nanotubes fibers	10^{-7}	10^{5}	1.3-2.0
Copper	1.7×10^{-8}	10^{7}	8.9
Aluminum	2.7×10^{-8}	10^{8}	2.7

Table 2-3 properties of CNT compared to other fiber materials [33]

2.6.1 Carbon Nanotubes Structure

The way the CNT-graphene sheet is warped into a cylinder decides many of its properties. Mainly, there are three forms of the CNT warping patterns, zig-zag, chiral or armchair, (Figure 2-7). The chiral vector defines the network structure for the CNT, and it is characterized by a pair of indices (n, m) and according to it the electrical properties of CNTs are defined.

(n) and (m) represent the number of unit vectors in the honeycomb crystal lattice of graphene along two directions. Generally, when m= 0, the nanotubes form is zigzag; when n = m, the nanotubes form is armchair; All the remaining forms are called chiral.

The nanotube diameter (d) is similarly determined by the chiral vector C = na1 + ma2, where a1 and a2 are the base cell vectors of graphite, while this vector specifies the direction of rolling a graphene sheet. Therefore, the diameter of a carbon tube can be calculated by

$$d = \frac{\sqrt[a]{m^2 + mn + n^2}}{\pi}$$

Where $a = 1.42 \times \sqrt{3}$ corresponds to the lattice constant in the graphite sheet.

And commonly, when n −m is a multiple of 3, then the nanotube is described as 'metallic' or highly conducting nanotubes; when it is not, the nanotube is a semi-metallic or semiconductor. At all times, the armchair form is metallic, whereas other forms could create a semiconductor nanotube.

For the multiwalled carbon nanotubes (MWCNT), they can be formed in two structural models: the Russian Doll model and Parchment model. When a carbon nanotube contains another nanotube inside it, it creates the Russian Doll model. However, when a single graphene sheet is coiled around itself manifold times, it creates the Parchment model [34].

Those extraordinary properties allowed CNTs to have many applications such as; Nano test-tubes, H2 storage media, batteries, field-emission materials, tips for scanning probe microscopy, chromatographic stationary phases, transistors, diodes, and carbon nanotube templates make superior metal nanoparticle supports because of their unique geometry, which can be used in sensors [29].

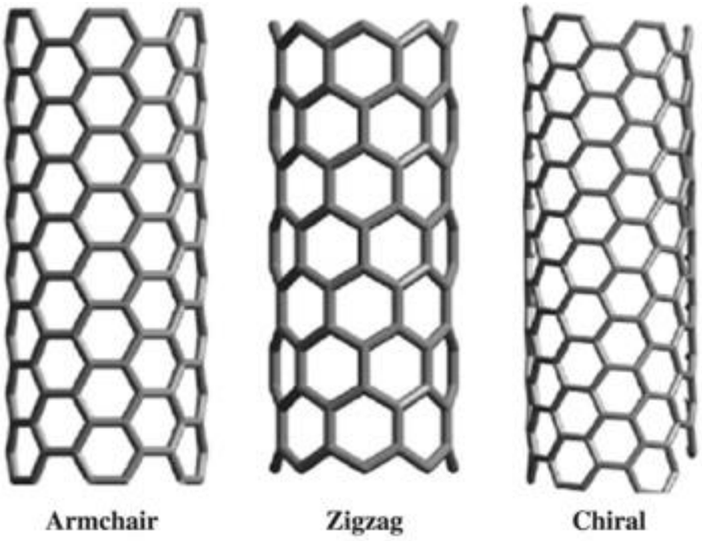

Figure 2-7 The different formations of the CNT sheet [35].

An older discovered type of carbon nanomaterials is vapor-grown carbon nanofibers (VCNFs). In 1889, a U.S. Patent was filed by Hughes and Chambers for vapor-grown carbon fibers. And in 1952 Radushkevich and Lukyanovich published the hollow graphitic structure for VCNFs. [36]. VNCFs have been widely investigated in the research and industry due to their low production cost and higher availability and outstanding, lower than CNTs, properties [30].

2.6.2 Synthesis Methods of Carbon Nanotubes

The raising interest in CNTs came as a result of the synthesizing of buckminsterfullerene C60, and other fullerenes, in 1985. It was the first discovery that carbon could form stable, ordered structures other than graphite and diamond. And the search was intense until the first type of CNTs was produced in 1991 [37].

Since then, many methods were tested and currently, CNTs have different techniques for the synthesis process. Each of those production mechanisms has its own properties and procedures. The three main methods can be summarized in the following:

1- Arc Discharge

Arc discharge is the most widely used technique for CNTs' synthesization, since in 1991, Iijima, while intending to produce fullerenes, observed CNTs in the carbon soot of graphite electrodes during an arc discharge, by using an electric current of 100 amps. Thus, Arc discharge became the first and consequently the most used production method.

Arc discharge is the electrical breakdown of a gas to generate plasma. There is a chamber that consists of two electrodes, one (anode) is filled with powdered carbon precursor along with the catalyst, usually, and the other (cathode) is usually a pure graphite rod, Figure 2-7. Inside the chamber, the gas or submerged inside a liquid environment fill it. Then an electrical current run through the electrodes, those electrodes generate an arc while kept at a gap of 1–2 mm to attain a steady discharge. A constant current is maintained through the electrodes to obtain a non-fluctuating arc, as fluctuation can affect the quality of the synthesized product. The arc current generates plasma of very high temperature around 4000–6000 K, which sublimes the carbon precursor filled inside the anode. CNTs self-assemble from the resulting carbon vapor. and drift towards the cathode to cool down. After several minutes, the discharge is stopped and cathodic deposit which contains CNTs along with the soot is collected. The deposit is further purified and observed under an electron microscope to investigate their morphology [32] [37].

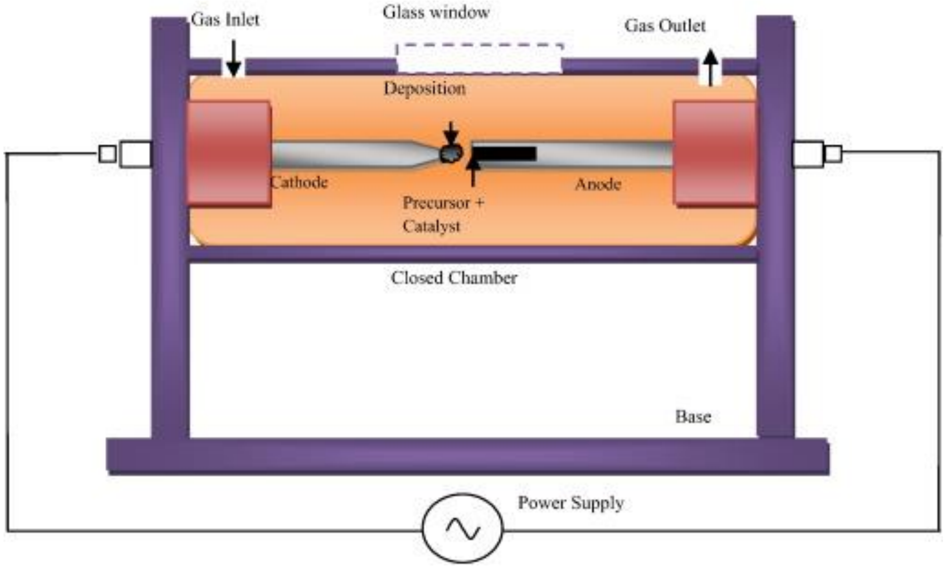

Figure 2-8 Schematic of an arc discharge setup [32].

2- Chemical Vapor Deposition (CVD)

The CVD technique uses the reaction of gases that contain carbon, such as hydrocarbons on a metal catalyst, at temperatures above 600 °C. The techniques of electric arc and laser ablation are quite similar, in that it is based on the condensation of carbon atoms from high purity graphite, the temperatures are significantly high, and differ in the degree of purity of the produced CNTs. CVD methods have a promising future in terms of price/unit ratio due to excellent heat and mass transfer ensuring a homogeneous product, inherent scalability, and comparatively low cost [37].

3- Laser Ablation

Laser ablation was the first technique used to generate fullerenes in clusters. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon-containing feedstock gas. Any amount of graphite could be vaporized by the laser irradiation under an inert atmosphere. Consequently, we can collect the CNTs after cooling down at the walls of a quartz tube.

In terms, of quality and production levels, arc discharge produces high amounts of impure material. While laser ablation produces a few pure CNTs. However, the chemical vapor deposition (CVD) method produces a poor quality of SWCNTs with a large diameter range which makes it difficult to be controlled. [37]. Other methods to produce CNTs include; flame synthesis, high-pressure CO disproportionation process, Hydrothermal synthesis, plasma torch method, solar energy, and electrolysis. Table 2-4 compares among the main methods [32].

Method	Arc discharge	Chemical vapor	Laser ablation

		deposition	
Established by	Ebbesen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Japan	Smalley, Rice, 1995
process	Connect two graphite rods to a power supply, place them a few millimeters apart, and throw switch. At 100 amps, carbon vaporizes and forms hot plasma	Place substrate in the oven, heat to 600 °C, and slowly add a carbon bearing gas such as methane. As gas decomposes its carbon atoms, which recombine in the form of CNTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the CNTs form;
Typical yield	30–90%	20–100%	Up to 70%
SWCNTs	Short tubes with diameters of 0.6–1.4 nm	Long tubes with diameters ranging from 0.6 to 4 nm	Long bundles of tubes (5–20μm), with individual diameter (1-2nm)
MWCNTs	Short tubes: inner diameter of 1–3 nm and outer of 10 nm	Long tubes with diameter ranging from 10 to 240 nm	No interest in this technique, due to costs but possible
Production	Easily produce both. SWCNTs have few structural defects; MWCNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWCNT diameter controllable, quite pure	Primarily SWCNTs, with good diameter control and few defects. The reaction product is quite pure

Table 2-4 comparison of the main methods of CNT synthesizing [37].

2.6.3 Carbon Nanotube Purification Methods

There are many methods of CNT purification depending on the followed synthesis technique. However, the following steps are shared among all purification procedures: deletion of large graphite particles and aggregations with filtration, dissolution in suitable solvents to eliminate catalyst particles and fullerenes, microfiltration and chromatography to separate and sort per size and remove the amorphous carbon clusters.

One method for the purification of MWNTs formed by arc-discharge techniques is by using oxidation techniques, which separate MWNTs from polyhedral graphite-like particles. The major drawback is the high destroying rate of starting materials (95%), as well as the low purity and the high reactivity of the remaining nanotubes at end of process.

Other nondestructive methods for CNT purification combine well-dispersed colloidal suspensions of tubes/particles with surfactants to prevent agglomeration.

There are many methods those include size exclusion chromatography and porous filters, as well as ultrasonically assisted microfiltration and most recently, boiling SWNTs in nitric acid or hydrofluoric acid aqueous solutions for purification of SWNTs, proved a degree of efficiency [34].

2.6.4 Dispersion Methods of Carbon Nanotubes

CNTs' dispersion method and quality are the most important factors on the final product of nanocomposites. The fact is that CNTs, without any dispersion, tend to agglomerate within polymeric or cementitious matrices and could lead to disadvantageous results on the nanocomposite rather than positive if it is not properly dispersed. Due to the presence of Van-der Waal forces and high surface area CNTs tend to form agglomerates. The high aspect ratios united with considerably good flexibilities results in a rise of the nanotube entanglement and close packing possibility [38].

The dispersion process is used to ensure a homogeneous spreading of the nanomaterials through increasing distribution and de-agglomerate the CNTs in the matrices. This dispersion process has two main patterns: Rupture, where the agglomerates split up into small size parts under high stress. Or erosion; where the agglomerate surface continues to lose small fragments detached due to lower stresses [30]. Figure 2-9 shows Scanning Electron Microscopy (SEM) images of poorly dispersed multiwall carbon nanotubes (MWCNTs) forming bundles in 18 h cement paste is shown below.

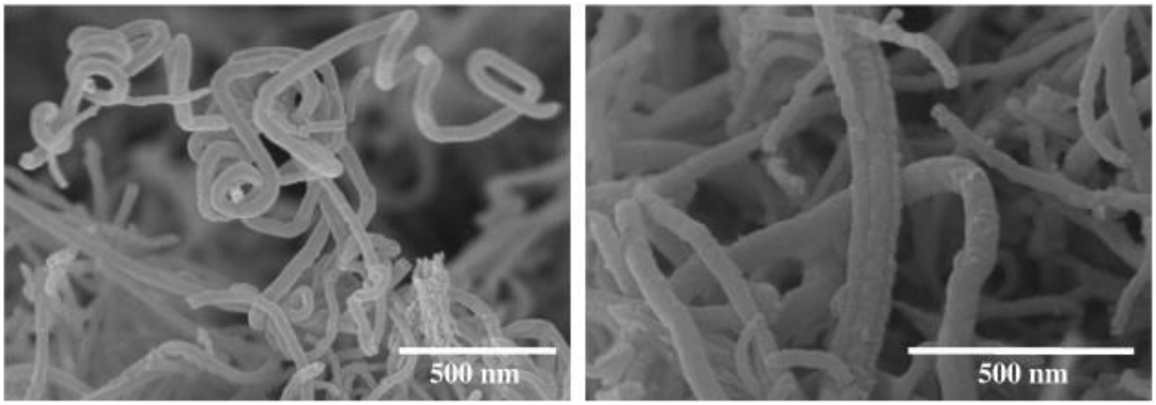

Figure 2-9 SEM images of poorly dispersed MWCNTs forming bundles in 18 h cement paste [39].

However, the behavior of CNTs dispersion has many aspects that define it, including the attractive forces, entanglement density, the length of nanomaterials volume fraction and matrix viscosity.

2.6.5 Techniques for CNTs Dispersion in Cementitious Composites.

The dispersion of CNTs in cementitious matrices is a critical issue, as the CNTs tend to agglomerate, due to Van der Waal attractive forces, affects the cementitious composite overall properties. The common method for mixing CNTs with cementitious matrices is to disperse these nanomaterials first in water. As other methods proved infeasible or decreased the outcome properties. As mixing CNTs, directly within cement mortar during mixing is not feasible, as the cement paste starts to harden and thicken within a short period after adding water. After mixing CNTs with water, the mixture of water and CNTs follow dispersion technique, and then the new dispersed mixture is added to the cement using a regular mixture. While dispersing CNTs in the water a careful attention should be directed that it would not interfere with the hydration and processing of cement nanocomposites.

Surfactants are amphiphilic molecules with a property of accumulation at surfaces or interfaces to promote stable dispersions of solids in different media. Those compounds work at the interface between immiscible bulk phases, such as oil and water, air and water or particles and solution, act to reduce the surface tension [38].

Many reasons can lead to low-quality dispersion, the lack of understanding of surfactant reaction, many surfactants that are successfully used to disperse carbon nanomaterials in polymeric matrices created defeats in cement hydration, entrap air in the cement paste or react with the water reducing admixtures. CNTs are separated by the cement grains; the presence of larger grains than the average leads to the absence of CNTs in some places, and high concentrations in other areas. Moreover, small grains of cement has many other disadvantages such as high water consumption, thermal cracking, more chemical and autogenous shrinkage, the right homogeneous distribution of cement particles is the best way to avoid any added aggregation [30].

The main techniques for dispersion can be divided into two main group approaches.

2.6.5.1 Chemical Methods

1- Surfactant: Surfactants can improve aqueous dispersion of nanomaterials by reducing the surface tension of water, and lead to stable dispersion as a result of electrostatic and/or steric repulsions among the surfactant molecules adsorbed on the nanomaterials surface. Yet, their ability depends on their concentration. Therefore, the optimal ration should be utilized to secure the best results. Also, the type of the surfactant has a huge effect on the CNTs' dispersion quality, from sodium deoxycholate (NaDC) to benzene sulfonate (SDBS), Triton X-100 (TX10), Arabic gum (AG), or cetyltrimethylammonium bromide (CTAB).

2- Use of cement admixtures: Polycarboxylate, which is commonly used as a superplasticizer within cement paste, was also found to be an effective dispersant of CNTs.
3- Covalent functionalization: One of the common approaches to enhance the dispersion of CNTs in water is the covalent functionalization. Covalent functionalization using acid mixture has been found successful to disperse CNTs individually within cementitious composites.
4- The combination of various chemical methods: The combination of some of the chemical methods can be more effective in few cases, for example, the combination of surface functionalization with polymers has been found to provide a more stable aqueous dispersion of CNT than using only polymers or functionalized CNTs. The dispersions of non-functionalized MWCNTs using acrylic acid polymer or gum arabic were found stable only up to 2 hours after which sedimentation was observed.

Many of the chemical methods cannot alone disperse nanomaterials in water; instead, they help in the dispersion process by wetting the nanomaterials with water and improving the dispersion stability. Therefore, there are always combinations of them and the physical techniques to acquire the best results [30][40].

2.6.5.2 Physical Methods

Ultrasonication - this technique consists of a device with a sink full of liquid medium (usually, water) using inside an electrical voltage converted to mechanical vibrations leading to formation and collapse of microscopic bubbles. During this process, millions of shock waves are created and a high level of energy is released, leading to the dispersion of nanomaterials in the liquid.

This technique is in need to be combined with other chemical routes to ensure dispersion quality. As alone it cannot secure a homogeneous distribution of CNTs within cement, meaning that a homogeneous nanomaterial dispersion in water does not guarantee a good dispersion in the nanocomposites as well [30].

2.6.6 Multiscale Incorporation Reinforcement

The incorporation of multiscale materials of Multi-Walled Carbon Nanotubes (MWCNT) and Microcrystalline cellulose (MCC) is a novel approach and a new research field, seeking such reinforcement systems with different configurations and dimensions lead to highly complex cementitious materials. Although, both materials have been investigated individually in previous research studies, yet this study is the first on the combination of them in a multiscale reinforcement.

The macroscopic material properties, such as compressive strength, ductility, and behavior, such as hardening, could always attribute to physical phenomena that happen on smaller multi levels. Those sub-scale phenomena are dominated by mechanisms across several length scales

The multiscale reinforcements have been studied extensively in different levels and different combinations, the micro/nano level was still relatively uninvestigated, though. Other multiscale studies showed positive influence in the developed composites. For example, the multiscale incorporation was reported effective in the case of a multi-scale fiber reinforced cement-based composite, as it improved the composted overall performance and increased loading rate, generates an increase in material modulus of rupture [41]. Also, the fabricated hybrid composites reinforced with carbon nanotube-coated carbon fabric showed great enhancement of the interlaminar shear strength, improved the out-of-plane mechanical and electrical properties [42].

Chapter 3

Dispersion of Multiwalled Carbon Nanotubes and Microcrystalline cellulose in Aqueous Suspension

3.1 Introduction

Carbon nanotubes are vastly utilized in plenty of industries [43], especially MWCNT as a carbon-based nanomaterial has many advantages. The same is valid for the cellulosic MCC as a natural and sustainable new substance. However, both materials have the natural tendency to aggregate if they are under non- homogeneous dispersion, resulting in the loss of their advantageous properties.

Until the present day, both materials are still relatively not fully investigated and the methods to prepare concentrated aqueous suspensions of either one of them are rare generally, while none on the preparation of a concentrated combination of MWCNT-MCC aqueous suspension. More precisely, the dispersion process in the most common techniques could need high surfactant concentrations, risking to reach the critical micelle concentration (CMC). CMC is affected by temperature, pressure and more importantly the surface moieties of substances like surfactants. When micelles format, any further amount of surfactants added to the system go to micelles and leads to CNT and MCC flocculation and agglomeration by forming aggregated or compound masses of particles on the surface of the suspension. If none or lower amount of surfactant is added, the dispersion process could require longer and more energetic mechanical stirring or/and ultrasonication, which could shred and break the MCC and MWCNT particles, causing a loss of the original inherent properties of these particles.

The Covalent techniques in the dispersion of nanomaterials have presented negative results on the MWCNT/MCC inherent properties. While on the other hand, the non-covalent functionalization techniques provide non-disruptive interactions between the nanomaterial surface and the medium through introducing a chemical bridging agent, the surfactants [44].

Different types of surfactants have been involved in the homogeneous dispersion of MCC-MWCNT materials. For MWCNT specifically, various surfactants have extensively studied to disperse them in cement or polymers. This includes ionic, nonionic and cationic surfactants such as sodium 4-dodecylbenzenesulfonate (NaDDBS), CTAB, sodium dodecane-1-sulfonate (SDS), Poloxamer 407 with trade name Pluronic® F68, Pluronic® F127, benzene sulfonate SDBS, and Triton® X-100. Although some of those ionic surfactants are known to disperse CNT well, such as SDBS, they could not be used in this research due to the presence of MCC. MCC is usually extracted through acid hydrolysis process leaving it with a negative charge of sulfate ions $(SO4)^{-2}$ on the surface. This charge would rebel with other negative charges of the ionic surfactants [45][46] [47].

Therefore, Cetrimonium bromide (CTAB) as a cationic surfactant has been selected for dispersing the MCC-MWCNT particles in the composite after considering the electron accepting nature of the amine head group. CTAB has also demonstrated to be the most efficient surfactant at neutral pH conditions for dispersing MWCNT particles as it enhanced their solubility levels [46].

Equally, Pluronic F-127 as a nonionic surfactant offered a homogenous effective dispersion of MWCNTs due to its amphiphilic structure. The main reason is the steric stabilization by the adsorbed surfactant. As the PEO chains of the Pluronic polymers extend into the water, and they impede nanotube aggregation [48] [40].

In the case of the MCC, the studies about dispersing it are relatively rare as an area that received limited attention. However, a previous study had a homogenous dispersion of MCC within cementitious composite was achieved using Pluronic F127 as a surfactant. Pluronic F127 represents a nonionic surfactant and it demonstrated negligible pH dependence. It possesses lower toxicity and biocompatibility making it more sustainable and appealing surfactant [27] [46]. Similarly, CTAB demonstrated efficient results with MCC dispersion [49].

All surfactants enhance the dispersion ability with increasing concentration till they reach a plateau, after that, any increase in concentration will diminish their properties and results in drawbacks to the suspension [46].

3.2 Materials and Methods

3.2.1 Raw Materials

This thesis includes two different rounds of experiments. However, for both the rounds of dispersion process, the main materials used were:

1- Multiwalled Carbon Nanotubes (MWCNT):

The multiwalled carbon nanotubes (MWCNTs) used in all experiments were supplied by Nanostructured & Amorphous Materials, Inc. (Houston, USA). The physical properties, like dimension and surface area, were obtained from the manufacturer, while purity and elements were specified using energy dispersive X-ray Spectroscopy (EDS using EDAX Si(Li) detector) with the 5kV acceleration voltage. All properties are presented in Table 3-1

Type of CNT	Diameter (nm)		Length (µm)	Surface Area (m²/g)	Elements (wt. %)		Impurity (%)
					C	O	
MWCNT	2-5nm (inner)	<8nm (outer)	10-30	350-420	92.1	7.9	0

Table 3-1 Properties of the used MWCNT

Figure 3-1 The properties of the used MWCNT

2- Microcrystalline Cellulose (MCC):

Microcrystalline cellulose (MCC) was provided by Sigma-Aldrich (Portugal), under the trademark Avicel® PH-101, with particles size of ~50 µm.

In the following Figure 3-2, the visual aspects of MCCs are presented.

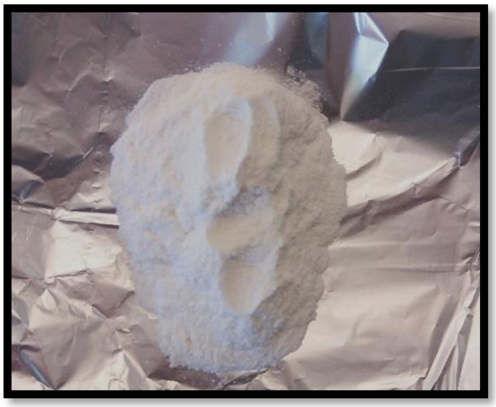

Figure 3-2 The visual aspects of the used MCC

3- Surfactants

Surfactants are used as surface-active agents to reduce the tension on the liquid surface, providing better spreading and low interfacial tension among the components surface. Any surfactant can be classified by the formally charged groups in its head [50].

Two types of surfactants were used in this research: cetyltrimethylammonium bromide (CTAB) alone in the first round and both CTAB and Pluronic F-127 separately in the second round. Pluronic F-127, chemical name Poloxamer 407, was supplied by Sigma-Aldrich (Portugal). As it does not have any charge groups in its head, it is identified as a nonionic. While CTAB has a positive charge, thus it is called cationic surfactant, was supplied by AppliChem GmbH Germany, under the trade number A6284,0250. Their chemical structures and properties are presented in Table 3-3.

Type of surfactant	Mol. Wt. (gmol^{-1})	Aqueous Solubility (at 25° C)	CMC* (wt.% at 25°C)
Pluronic F-127	12600	>10%	0.004–0.091
CTAB	364.46	0.3%	0.034

Table 3-2 Main properties of CTAB and Pluronic F-127 * The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC.

Figure 3-3 presents the visual aspects of the used Pluronic F-127 and the used CTAB, while Figure 3-4 illustrates the chemical structure of both used surfactants.

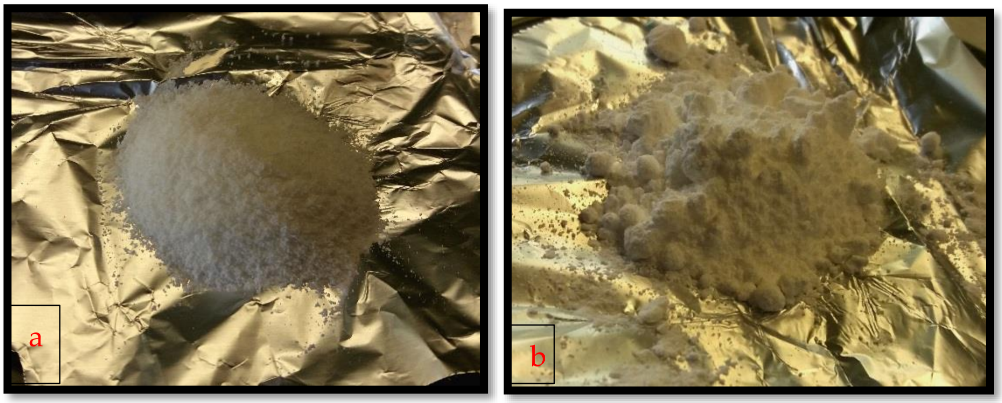

Figure 3-3 The visual aspects of the used a) Pluronic F-127, b) CTAB

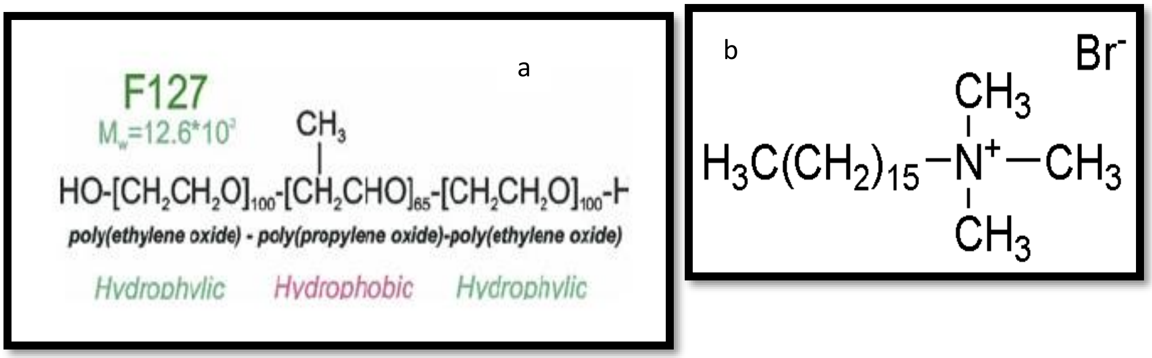

Figure 3-4 The chemical structure of used surfactants a)Pluronic, b) CTAB [51].

4- Tributyl Phosphate (TBP)

Tributyl phosphate is an organophosphorus compound, a solvent, and a plasticizer. It has the chemical formula $CH_3CH_2CH_2CH_2O)_3PO$, and was provided by Chem-lab (Belgium), under the name (Tributyl phosphate v.p). The properties are presented in Table 3-3.

Name	Chemical formula	Mol Weight (g/mol)	Density g/ml
Tributyl phosphate	C12H27O4P	266.32	0,97

Table 3-3 Properties of TBP

The role of tributyl phosphate was as a defoaming agent, to decrease the air bubble in MCC-MWCNT cementitious reinforced composite [52].

In the addition to the previously mentioned materials, other basic materials were provided by Fibrenamics laboratory including distilled water, superplasticizer and others.

3.2.2 MCC-MWCNT Dispersion Route in Aqueous Suspension

The utilized method for dispersing MWCNT and MCC was a combination of chemical and physical dispersion methods. To achieve a good dispersion, firstly MCC powder was added to water for 24 hours to ensure its fine mixing; later MWCNT powder, with a certain amount of the surfactant, was added to water; then the mix was subjected to magnetic stirring for 15 minutes. After that, the suspension was sonicated in the bath sonicator (Ultrasonic Cleaner 3200 S3, Sonica, CP 230T) for 30-60 minutes, at 45 kHz frequency and 80 W power and complete process was performed at room temperature. The main aim of this hybrid route is to preserve the inherent properties of both MCCs and

MWCNTs and to present it as a practical sustainable method due to its low energy consumption and short duration. All used glassware was rinsed and cleaned to ensure the accurate measurements.

3.2.3 Characterization of MCC-MWCNT Dispersion

Three main techniques were used to identify the properties of MWCNT-MCC suspensions.

3.2.3.1 Visual Observation

The suspensions of MWCNT-MCC were stored in small 25ml vials and monitored for 24 hours to detect any sedimentation, as bundles of MCC and/or MWCNT could create residues at the bottom.

3.2.3.2 Optical Microscopy

Each of the samples needed to be inspected and analyzed. An optical microscope (Olympus BH2 Microscope) was used as its observation reveals if MCC and CNTs were dispersed homogeneously in the suspensions or not. The focus of the lenses was 1.67 for the upper lens, and magnification 10x for the lower lens directed on the specimen on a glass slide. Several pictures were taken for the same suspension, yet in different drops, to ensure well average homogeneity and better assessment.

3.2.3.3 UV-Vis Spectroscopy

The ultraviolet-visible spectrophotometry, UV-Vis spectroscopy, (UV 2401 PC, Shimadzu) was used to evaluate the dispersion quality and the absorbance of MWCNTs and MCCs in the aqueous surfactant solution. The applied wavelength region was between 190 and 1000 nm, in this wavelength region MWCNT and MCC clusters are inactive usually, due to photoluminescence quenching, creating a weak and broad signal.

A calibration curve of absorbance and concentration was used to measure the dispersion quality of each MCC-MWCNT suspensions. However, these curves needed two types of solutions, reference samples from MWCNT-MCC suspensions diluted in water. Moreover, to eliminate the peaks resulted from the surfactant in the measurement, subtracting equivalent concentration surfactant that was added to the MWCNT-MCC suspensions were used as blank samples.

The concentration of dispersed MWCNTs was used to calculate the ratio of dispersed MWCNT concentration over the initial MWCNT concentration, this ratio is called extractability and can be calculated as follow:

$$E\text{xtractability} = 100\times \frac{\text{concentration } of\ dispersed\ MWCNT}{\text{concentration } of\ initial\ MWCNT}$$

In the UV-VIS spectroscopy, the absorbance has no unit. Also, the absorbance depends basically on the concentration of the sample solution and the length of the wave.

3.3 Results and Discussion

3.3.1 First Round

The concentrations of MWCNT and MCC along with CTAB are presented in the following Table 3-4. The concentrations of the component in the dispersion route are given with respect to water. The main goal was to optimize the concentration of the MCC, MWCNT, and surfactant (CTAB) to determine the ideal percentages to be used.

Sample name	CTAB surfactant concentration	MWCNT concentration	MCC concentration
1	=20% MCC+ 100% MWCNT	0.2%	0.4%
2	=20% MCC+ 100% MWCNT	0.6%	0.4%
3	=20% MCC+ 100% MWCNT	0.2%	1%
4	=20% MCC+ 100% MWCNT	0.6%	1%
5	=20% MCC+ 100% MWCNT	0.2%	1.5%
6	=20% MCC+ 100% MWCNT	0.6%	1.5%
7	=40% MCC + 100% MWCNT	0.2%	1.5 %
8	=60% MCC + 100% MWCNT	0.2%	1.5 %
9	=80% MCC + 100% MWCNT	0.2%	1.5 %
10	=100% MCC + 100% MWCNT	0.2%	1.5 %

Table 3-4 First round used samples concentrations

3.3.1.1 Visual Inspection of Sedimentation

The condition of various MWCNT- MCC suspensions dispersed using CTAB, within 24 hours of their preparation is shown in Figure 3-5 The samples went through the full dispersion method from mixing with a surfactant to mechanical stirring and ultrasonication.

Samples suffered from a variety of sedimentation levels as MCC-MWCNT bundles flocculated under the gravity force. Generally, samples with lower concentrations of MCC and MWCNT showed better dispersion as can be seen in samples of 0.4%MCC with 0.2%MWCNT and 0.6%MWCNT. In the second one 0.4%MCC + 0.6%MWCNT a better dispersion was achieved as the surfactant amount increased as it is a function of MCC and MWCNT. Higher concentration as in 1.5%MCC samples had large clusters of MCC-MWCNT which were not dispersed settled down in the bottom of the vial. In addition, well-dispersed MWCNTs or MCCs could also re-agglomerate and form bigger clusters and flocculate, with the time if not directly mixed with the cement.

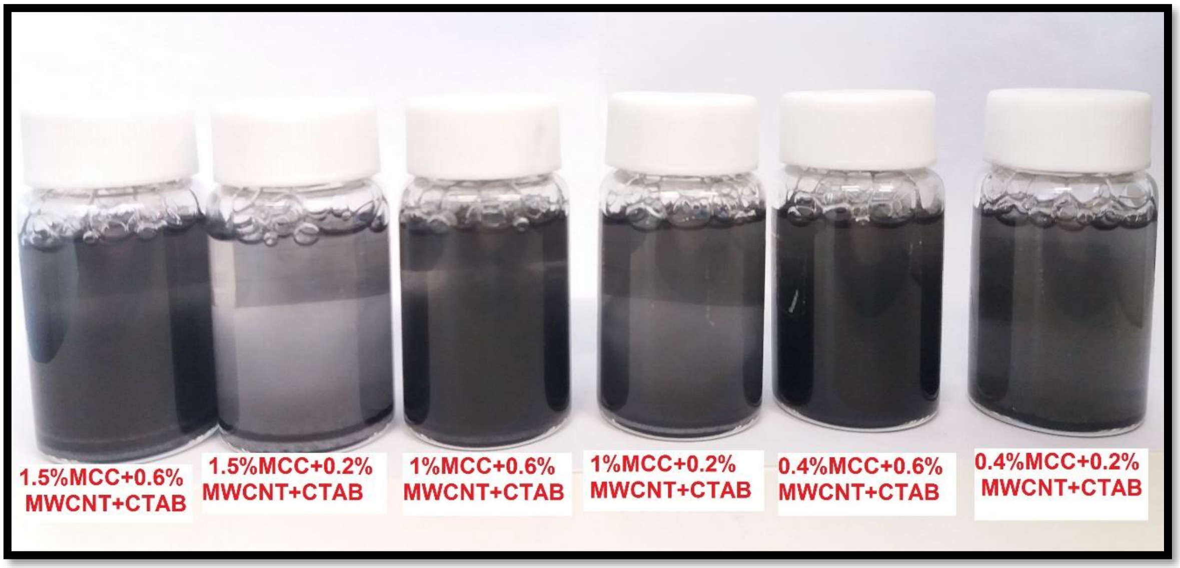

Figure 3-5 Visual observation of sedimentation of various MCC-MWCNT suspensions prepared with CTAB.

3.3.1.2 Optical Microscopy

The optical micrographs of the first round of MWCNT-MCC and CTAB suspensions are shown in Figure 3-6

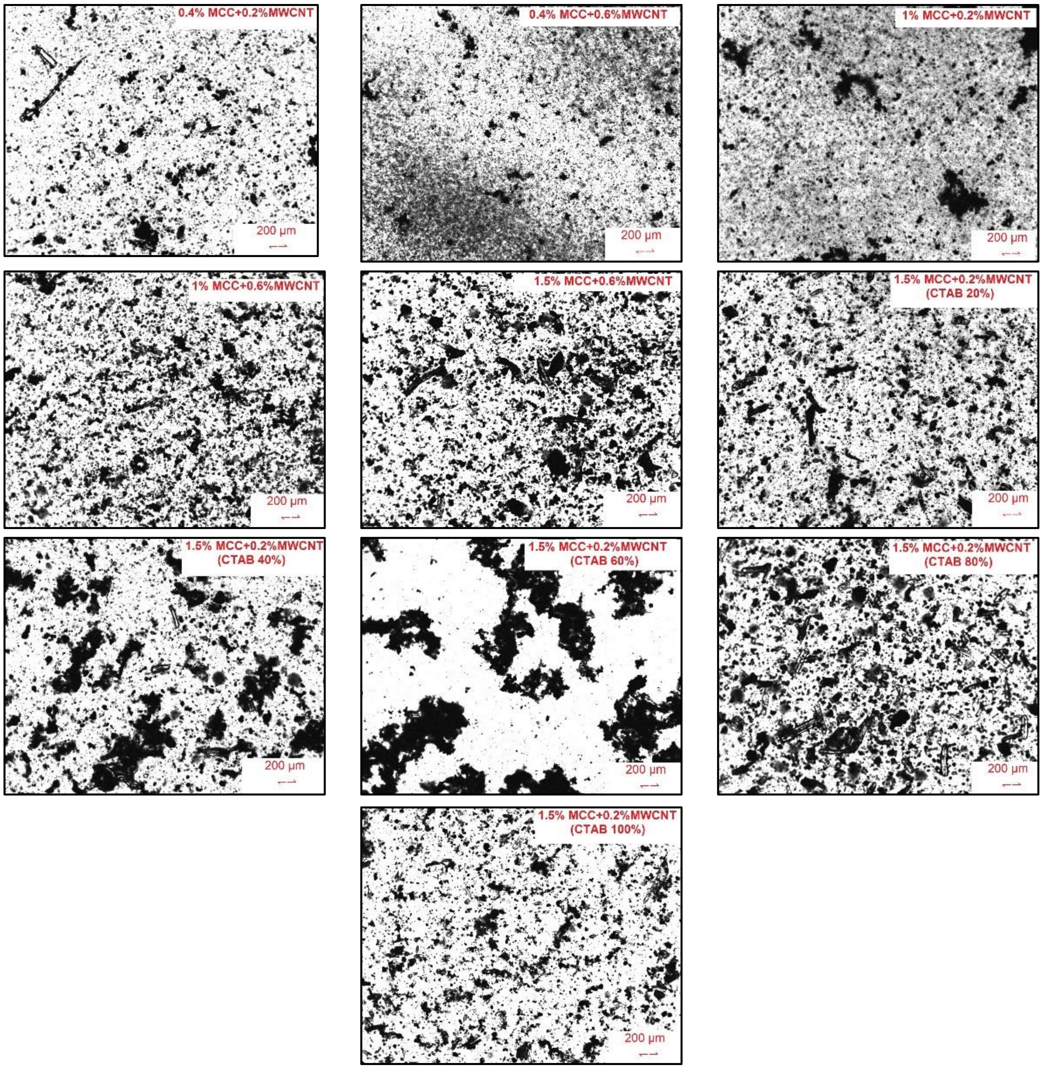

Figure 3-6 Optical Micrographs of first-round samples

In the graph of Figure 3-6, informative results can be obtained in general. The homogeneity of the dispersion was dependent on the MCC and MWCNT concentrations. Lower percentages of MCC and MWCNT gave better results apart from the surfactant concentration. In the samples of 0.4% MCC + 0.2%MWCNT + CTAB and 0.4% MCC + 0.6%MWCNT + CTAB a good dispersion can be noticed. On the contrary, more agglomerations are detected in 1% MCC + 0.2%MWCNT + CTAB samples and the case is slightly better in 0.4% MCC + 0.2%MWCNT + CTAB samples. Overall, we observed that higher the amount of the MCC resulted in higher levels of agglomerates and clusters as seen in the 1.5 %MCC samples.

Regarding the concentration of the CTAB, as can be seen, the lower the percentage of the CTAB of (20% w.r.t MCC, with consistent 100% w.r.t MWCNT) had the best dispersion while the higher of (40%, 60%, 80%) had higher agglomeration rates and formations of

MCC and MWCNT bundles. Although the 100% CTAB samples had a relatively improved dispersion and higher homogeneity level, yet it resulted in foams and bubbles that could deeply affect the properties of the composite during the molding process as air voids.

3.3.1.3 UV-Vis Spectroscopy: Absorbance

The UV-Vis absorption spectra curves for MCC-MWCNT suspensions are provided in Figure 3-7 The UV-Vis spectra are of the suspensions prepared by dilution of the concentrated original suspensions.

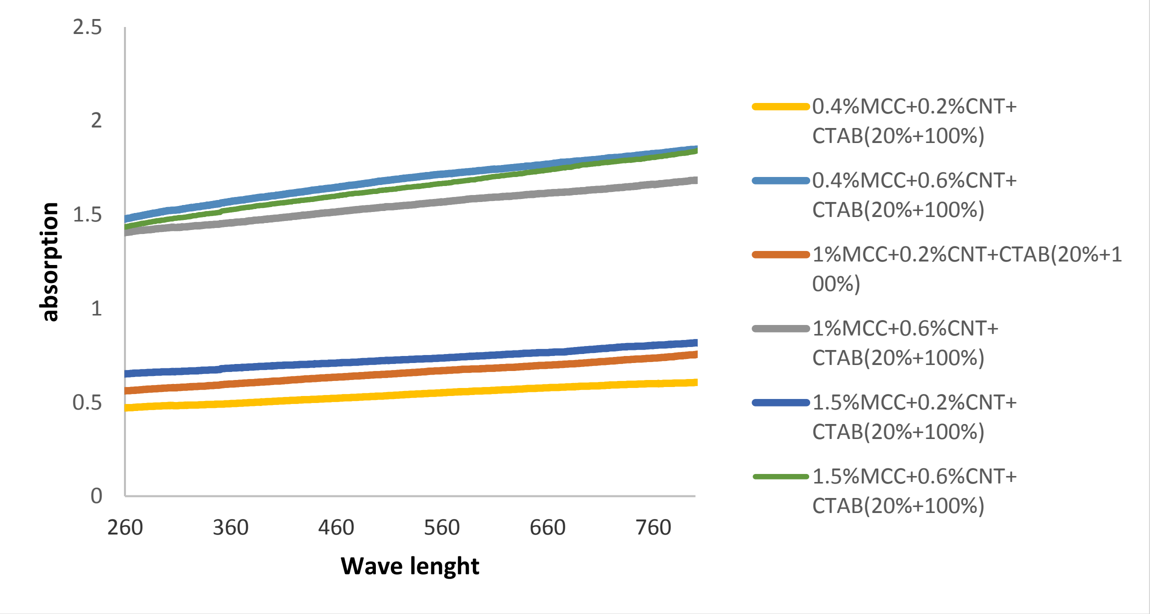

Figure 3-7 Absorbance curves of UV-VIS spectroscopy test for first-round samples.

The graph represents the absorptions for each sample. The less concentration of the MCC and MWCNT samples resulted in the lower absorption rates, which could be interpreted that the suspension could still tolerate higher concentrations of MCC and MWCNT. The 0.4%MCC + 0.6%CNT + CTAB samples lead to a very high absorption which could be a result of the high homogeneity among the three components. In the 1.5%MCC + 0.2%CNT + CTAB samples, a clear reduction of the absorption could be seen. It is also concluded that the higher MWCNT concentration led to higher absorption in general till reaching a plateau point.

3.3.2 Second Round

The concentrations of MWCNT and MCC along with added CTAB/Pluronic F127 are presented in Table 3-5, where all concentrations are with respect to water.

Sample name	Type of surfactant	Surfactant concentration	MWCNT concentration	MCC concentration
1	CTAB	=40% MCC+100%MWCNT	0.2%	0.4%
2	CTAB	=20% MCC+100%MWCNT	0.6%	1%
3	Pluronic	3%	0.2%	0.4%
4	Pluronic	5%	0.2%	0.4%
5	Pluronic	3%	0.6%	1%
6	Pluronic	5%	0.6%	1%

Table 3-5 Second round used samples concentrations

3.3.2.1 Visual Inspection of Sedimentation

The samples of MCC-MWCNT suspensions after 24-hour preparation with both surfactants are shown in Figure 3-8, for visual observation.

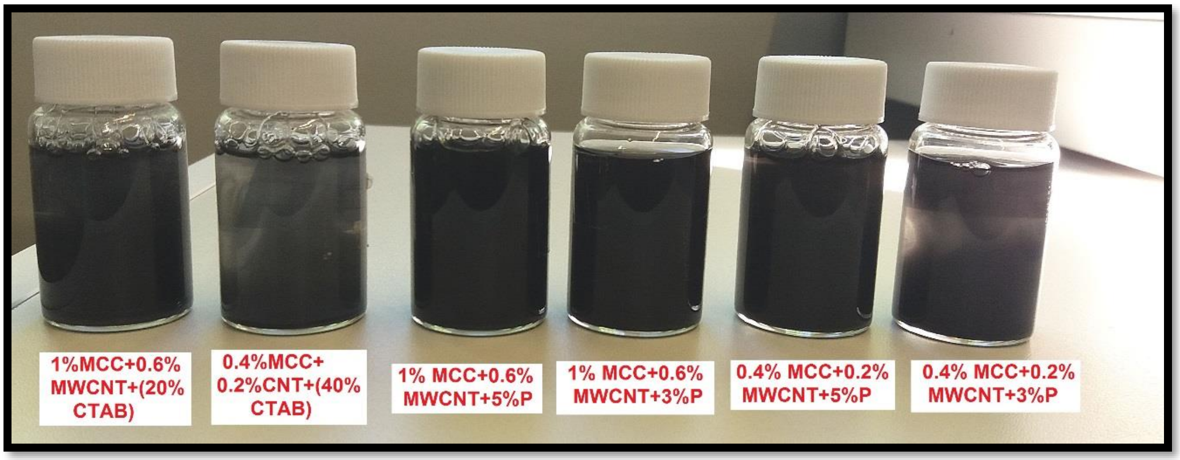

Figure 3-8 Visual observation of sedimentation of various MCC-MWCNT suspensions prepared using CTAB and Pluronic.

Overall good dispersion is seen in the second-round samples as optimized concentration and good dispersion led to a better stability of the suspension. The 1%MCC samples prepared using Pluronic F-127 achieved very good dispersion with no noticeable sedimentation. The same is with 1%MCC samples prepared using CTAB. Slight sedimentation could be seen with the 0.4%MCC samples prepared using either CTAB or Pluronic. This could be explained due to re-agglomeration of MCC-MWCNT clusters as the surfactant concentration in its lower percentage, the 24 hours could motivate re-agglomeration although the samples were well dispersed freshly after prepared.

3.3.2.2 Optical Microscopy

The Figure 3-9 presents the optical micrographs of the second round of MWCNT-MCC dispersed with CTAB /Pluronic F-127suspensions.

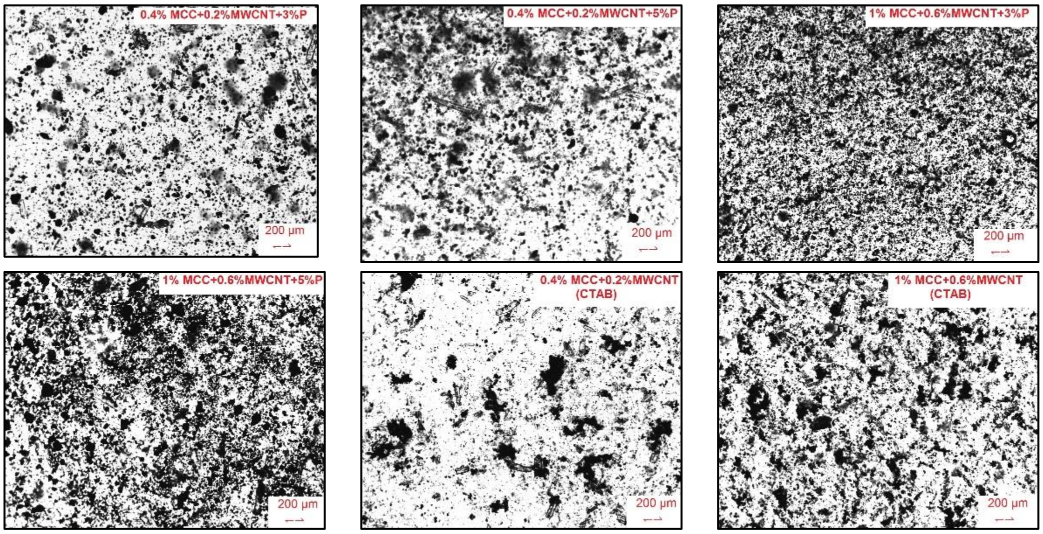

Figure 3-9 Optical Micrographs of second-round samples

In the second-round, the optical microscopy was conducted to identify the best concentration of Pluronic F-127 to be added. Previous studies showed that concentrations around 5% were good with CNT suspensions. However, in our case, the combination has two types of components, MCC and MWCNT. The mechanism they react with is not clear for us. Thus, we used 3% and 5% concentrations of Pluronic F-127 for the first four samples in the second round.

The dispersion quality is noticeable in the low concentrations of the MCC and MWCNT. However, we can detect that the 3%P samples dispersed the MCC and MWCNT better in comparison with the 5% samples. in the 0.4%MCC + 0.2%MWCNT + 3%P samples, few bundles can be spotted, yet with higher concentrations of Pluronic F-127 in 0.4%MCC + 0.2%MWCNT + 5%P. The same could be stated for the 1%MCC + 0.6%MWCNT + 3%P and 1%MCC + 0.6%MWCNT + 5%P despite the higher concentration of MCC and MWCNT.

For the other two samples, to confirm what was concluded from the first round we can see that both 0.4%MCC + 0.2%MWCNT + CTAB and 1%MCC + 0.6%MWCNT + CTAB samples had appropriate dispersions.

3.3.2.3 UV-Vis Spectroscopy: absorbance

The UV-Vis absorption spectra and calibration curves for the second round of MCC-MWCNT suspensions are provided in Figure 3-10. The UV-Vis spectra are for the suspensions prepared by dilution of the concentrated original suspensions.

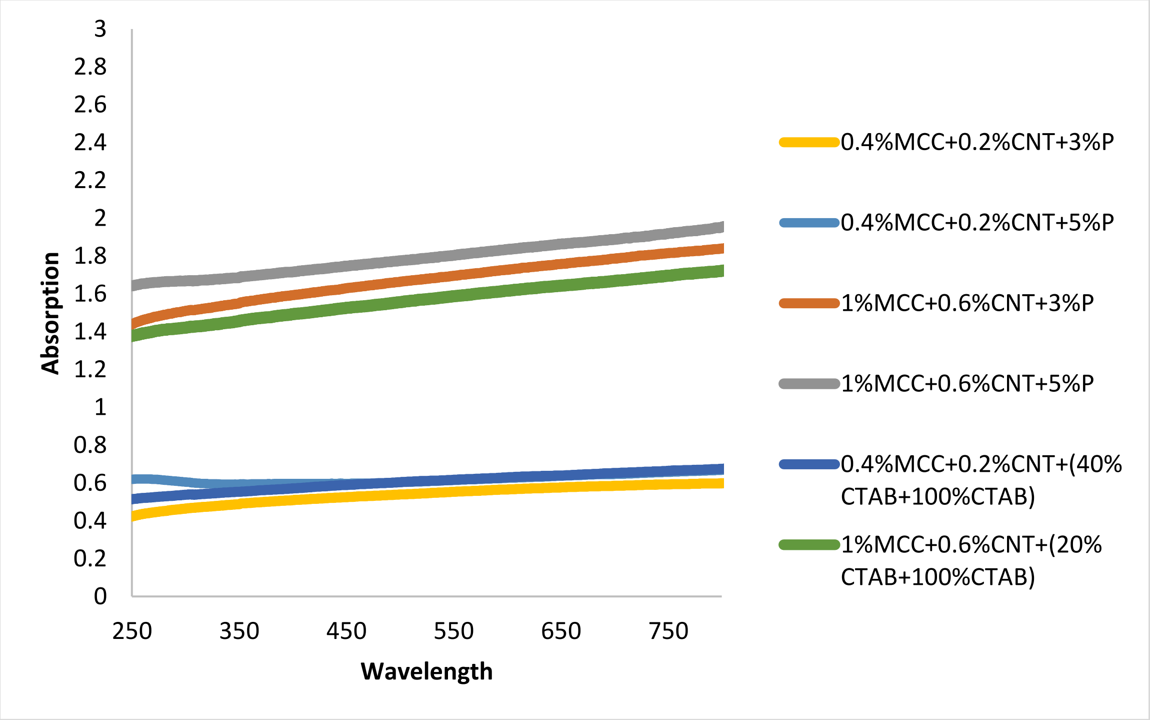

Figure 3-10 Absorbance curves of UV-VIS spectroscopy test for second-round samples.

In the second-round curves, a similar absorption trend is easily seen. In all cases with 0.4% MCC, apart from the MWCNT concentration, the absorption was relatively lower below 0.8. This is valid for the 0.4%MCC samples wither they were dispersed using 3%, 5% Pluronic F-127 or CTAB. Thus, we can conclude that the addition of Pluronic F-127 positively influenced the sample by improving the absorbance despite that the needed Pluronic F-127 was in much higher concentrations as compared to CTAB.

On the other hand, the 1% MCC samples showed higher absorption, with the 1%MCC + 0.6% CNT + 5%P ranked first and followed closely with the 1%MCC + 0.6% CNT + 3%P samples. The 1%MCC + 0.6% CNT + CTAB was placed the third with absorption around 1.4 absorbance unit at a wavelength of 250 nm.

3.4 Discussion: MCC and MWCNT Dispersion in Aqueous Suspension with the Aid of Surfactants - Pluronic F-127 and CTAB.

The quality of the MCC and MWCNT particles dispersion is dominated by the absorption of the surfactants as well as the optimal concentrations of the three components. The MCC-MWCNT suspensions were under the influence of the type of the surfactant as its results differed from the cationic CTAB to the nonionic Pluronic. Each specific surfactant suspension faced direct and indirect challenges to disperse different particles. MCCs have larger dimensions at the micro level, while the MWCNTs are comparatively lower at the nano level. This tested each material disperse-ability and each surfactant ability to produce a homogenous suspension. MCC created larger agglomeration requiring more intensive dispersion tools (longer mechanical stirring/ultrasonication) to ensure adequate results. This extended ultrasonication increased the shattered MCC particles as seen under the Optical Microscope. While in other studies [46], MWCNT particles required certain concentration of Pluronic, the new multiscale combination was craving for significantly higher concentrations of Pluronic F-127 to reach 3% w.r.t water. Thus, the mechanical stirring was crucial for the Pluronic F-127 samples as the Pluronic F-127 tended to form clusters shortly which could severely harm any composite by creating voids in the structure.

Further challenges were faced with the rapid stabilization and in some cases sedimentation of MCC-MWCNT particles in the bottom of the suspensions. As it was noticed visually, and in the UV-VIS test, the MCC particles gravitate the MWCNT particles to settle down in comparatively short time (24-48 hours). This interpreted with the need to perform mechanical stirring before any molding or mixing with the cement elements to ensure the homogeneity of the suspension is all areas. Yet, longer stability may be predictable with the use of Pluronic F-127 due to the stability of the long molecules sitting on the MWCNT surface, keeping it absorbed for longer periods and delaying the re-aggregation of the nanotubes.

An interesting observation is the links between the high MCC-MWCNT concentration and the moderate percentage of surfactant to achieve higher absorbance in UV-Vis compared to the lower concentrated MCC-MWCNT suspension. Higher concentrations led to higher absorbance, yet less dispersion quality. Furthermore, the higher the MCC-MWCNT concentration, the lower the need of CTAB to be added as the CTAB is directly related to the MCC and MWCNT concentrations. However, in the case of Pluronic, there is a negligible influence of the MCC and MWCNT amount on the Pluronic F-127 amount. To achieve the maximum absorbance and to prevent large agglomerates, an optimal percentage of surfactant should be added, lower or higher than this percentage will have a negative effect on the suspension properties (absorbance, dispersion).

3.5 Conclusions

This chapter focuses on studies of different concentrations of MCCs and MWCNTs with two different kinds of surfactant to obtain homogenous suspensions of MCC-MWCNT in an aqueous medium. Two types of surfactant were utilized, CTAB in the first round and CTAB and Pluronic F-127 individually in the second round to prepare the suspensions along the physical dispersion techniques of mechanical stirring and ultrasonication. We investigated the influence of the MCC-MWCNT concentration as well as surfactant's type and concentration on the properties of the new composite.

The dispersed suspensions were tested for the MCC-MWCNT agglomerations, sedimentation, and absorbance. The main goal of first-round of experiments was to obtain more detailed information about the optimum concentration of the surfactant and MCC-MWCNT. The use of higher MWCNT and MCC concentration, until a peak limit, with optimal surfactant concentration, resulted in good homogenous dispersion, as in 1%MCC + 0.6%CNT with 3%P or CTAB samples. Although the less concentrated samples showed lower absorbance, they presented better dispersion pattern under the optical microscope lens.

Chapter 4

Development of Multiwalled Carbon Nanotube and Micro Crystalline Cellulose Reinforced Cementitious Composites

4.1 Introduction

Carbon nanotubes and particularly MWCNTs are considered exceptional materials for their many advantageous properties. With the fact of being the strongest material in the world, MWCNT has proved to be vastly useful and promising in several industries. The researchers in civil engineering, in general, and those working in concrete sector specifically were keen to utilize it as well. However, the hardest challenge for the development of high-performance MWCNT reinforced composites is the proper dispersion of the MWCNT in the cementitious matrices.

MCCs as well have attracted many researchers and industries to invest in, due to their sustainable properties as biobased natural fibers, degradability, and the relatively low cost. MCC has been studied mainly in reinforcing polymeric and it demonstrated remarkable results. Although MCCs have excellent physical and mechanical properties (tensile strength 7.5 GPa, axial elastic modulus up to 200 GPa), however, when MCC was incorporated to reinforce cementitious composite, no significant mechanical properties enhancement was reported [9]. The main suspected reason is that MCC was not dispersed at all before being incorporated into the cementitious matrix. Yet, the challenge with MCC is not only the quality of the dispersion, but the material usage as a cementitious composite reinforcement suffers from the lack of studies and holistic research on its properties.

As could be concluded, both MCC and MWCNT are dependent on the quality of their dispersion to influence positively the cementitious composite as their agglomeration can damage the efficiency of them as reinforcements. The method of dispersion MCC/MWCNT within the mortar directly proved not applicable as the cement paste starts thickening shortly after adding water. Thus, the used approach is to mix and disperse MCC-MWCNT within the water firstly before being mixed with the other ingredients of the concrete [40].

The followed technique in this research in preparing the homogeneous aqueous dispersion of MCC-MWCNT is evidently more sustainable, due to the combination of various physical and chemical techniques in the same time. Through the two cycles of experiments, the physical methods (ultrasonication and mechanical stirring) have been used along with the chemical methods by adding two types of surfactants. Pluronic F-127 and CTAB were selected as the surfactants used to produce MCC-MWCNT reinforced cementitious composites. By applying this combined method, we eliminated the opportunity of damaging the MCC/MWCNT particles by following long dispersion chemical techniques or the chance of high energy consumption that is associated usually with the physical methods.

As discussed before in Chapter 3, CTAB was used as a surfactant in the first round of the experiments both to disperse MCC-MWCNT and to develop the cementitious composite reinforced by them. In the second round, optimized concentrations of CTAB and Pluronic F-127 were used separately to achieve the last results.

4.2 Materials and Methods

4.2.1 Raw Materials

In addition to the raw materials used for the dispersion (MWCNT, MCC, CTAB, Pluronic F-127), the following materials were used for the sake of preparing the MCC-MWCNT mortar composite.

1- Stander Sand

The CEN standard sand was provided by Société Nouvelles du littoral Lab, France, with Certificate EN 196-1. It is a natural sand, which is siliceous particularly its finest fractions. It is clean and dried with generally isometric particles and rounded in shape. The grading measured by the manufacturer. The sifting properties for sand particles are listed in Table 4-1 following the requirements of EN 196-1 and ISO 679: 2009.

Square Mesh Size (mm)	**Cumulative (%)retained**
0.08	**99 ± 1**
0.16	**87 ± 5**
0.50	**67 ± 5**
1.00	**33 ± 5**
1.60	**7 ± 5**
2.00	**0**

Table 4-1 the sizes of the sand particles

2- Ordinary Portland Cement

The used cement was ordinary Portland cement CEM I 42.5R provided by the construction materials laboratory at the University of Minho and manufactured by SECIL, Portugal. This cement was used to produce all the composites samples and was maintained under dry and clear conditions to ensure the quality of mixing and final properties. The main properties of this cement are listed in Table 4-2.

Composition	95-100%clinker, (0~5% minor additional materials)
Insoluble residue	≤ %5
Sulfur trioxide (SO3)	≤ %4
Chloride (Cl-)	≤ %0.1
Loss on ignition	≤ %5
Initial setting time	≥ 60 minute
Soundness	≤10 minute
2 days compressive strength	≥ 20.0MPa
28 days compressive strength	≥ 42.5MPa ≤ 62.5MPa

Table 4-2 The main chemical and mechanical characteristics of the used Portland cement

4.2.2 Preparation of MCC-MWCNT Aqueous Suspensions

In both rounds the method for preparing the suspensions was similar; after adding the MCCs, the MWCNTs and the surfactant (CTAB in the first round and CTAB or Pluronic F-127 in the second round) the defoamer TBP was added. Then a magnetic stirring for 15 minutes was made to ensure homogeneous mixing, followed by ultrasonication (Ultrasonic Cleaner 3200 S3, Sonica, CP 230T) operated at 45 kHz frequency, for 30 minutes. The results were the MCC-MWCNT well dispersed in the aqueous suspensions.

To optimize the concentration of the TBP defoamer to be added with the CTAB samples, two sets of samples were prepared with different concentrations of TBP (75% and 100% of CTAB weight), while only 50% of Pluronic F-127 weight equivalent of TBP was added to the Pluronic F-127 samples based on previous studies [40].

4.2.3 Preparation of MCC-MWCNT Cementitious Mortars

In the second stage, to prepare the cementitious composites, the MCC-MWCNT suspensions were mixed with the cement (cement/water ratio of 0.5) and the sand (1350 gr) in a Hobart mixer. After the proper mixing, the samples were molded in standard rectangular molds that have the dimensions of 160 mm* 40 mm* 40 mm. The molded samples were kept in a moist environment for 48 hours before they were demolded. The demolded samples then were saturated in the water either for 28 days or 56 days to complete the hydration process and investigate its influence on the mechanical properties.

4.2.4 Characterization of Plain Cement Mortar and MCC-MWCNT Composites

4.2.4.1 Workability

One of the important characteristics of cement mortar is the workability. To identify it, the consistency of the materials which is the measure of fluidity and so the workability, need to be assessed.

To evaluate the consistency of the MCC-MWCNT fresh mortar pastes, the flow table method was followed. The flow table, mini slump test, is based on determining the diameter of the mortar paste at two perpendicular directions. First, the fresh mortar will be filled in a truncated mini-cone on three levels to ensure no air gaps, then the mini-cone will be removed and the material will flow reaching a steady state and a final diameter.

4.2.4.2 Flexural Strength

To determine the flexural behavior of the samples, the three-point flexural test was conducted. This test provides information about the ductility, flexural stress, and the material's strain. It is an easily performed test, however, a special attention to the sample loading geometry should be paid.

To further investigate the fracture behavior, flexural tests were also performed on the plain mortar and MCC-MWCNT mortar samples, as demonstrated in Figure 4-1. The flexural test machine provides tensile stresses on the convex side of the sample and compression on the concave side, creating shear stress along the span of the sample. The shear stress should be kept minimal to ensure the primary failure is from the tensile stress, thus is performed by obtaining the right span/depth ratio, for our samples it was ¼.

Figure 4-1 The three-point flexural test machine

4.2.4.3 Compressive Strength

Compressive strength measuring is the most common examination for hardened concrete, as it is a vital property in cementitious composite, considering that concrete possesses high compressive strength usually and it is taken as the main compressive strength in the design process. Thus, compressive tests were performed on all the samples to identify their compressive behavior. Figure 4-2.

Figure 4-2 The compressive machine with a sample under distributed pressure.

4.2.4.4 Mercury Intrusion Porosimetry

For the evaluation of porosity characteristics in cement-based materials, many techniques are applied. However, Mercury Intrusion Porosimetry (MIP) is widely used as it is performed in suitable conditions and has reliable results [53].
Mercury Intrusion Porosimetry (MIP) is a common indirect technique for identifying the distribution of pore sizes in cementitious composites. The relationship between the pressure and capillary diameter is:

$$P = \frac{-4\gamma \times \cos\theta}{d}$$

Where; P represents the pressure,
γ= surface tension of the liquid,
θ= contact angle of the liquid,
d= diameter of the capillary.

The pore size distribution is determined from the volume intruded at each pressure increment. However, the total porosity value is calculated by summing the total volume intruded [54].

4.2.4.5 Dry Bulk Density

According to the European standards BS EN 1015-10:1999 The dry bulk density of a hardened mortar sample is determined as the quotient of its mass in oven dried condition, and the volume which it occupies when submerged in water in a saturated condition. So, it is the weight of the many particles of the composites divided by the volume the particles occupy [55].
The steps to determine the bulk density of a sample are:
1-To calculate the dry bulk density of a sample, the following should be firstly calculated:

The mass of the specimen, m=Ms,dry (kg). Which is the constant mass of the sample that is reached by drying the specimen at 70 C, until the two-consecutive weighing, 2h apart during the drying, has less than 0.2% difference in the mass of the dry sample.

2- Calculate Vs

$$Vs = \frac{\mathrm{Ms, sat} - \mathrm{Ms, i}}{\rho \mathrm{w}}$$

Where; Ms,sat is the mass of saturated specimen of hardened mortar (kg)

Ms,i is the apparent mass of saturated specimen of hardened mortar immersed in water (kg)

ρw is the density of water (kg/m^3).

Vs is the volume of the specimen of hardened mortar (m^3).

3- The ratio of the recorded mass, Ms,dry, to the volume Vs represents the dry bulk density.

4.2.4.6 Thermo-gravimetric Analysis

Thermogravimetric Analysis (TGA) is a branch of thermal analysis, which studies the physical and chemical properties of samples as a function of temperature with constant increasing heating rate or as a function of time with constant temperature or constant mass loss [56].

TGA for MCC-MWCNT mortar and plain mortar samples was performed utilizing Simultaneous Thermogravimetric Analyzer (STA) Hitachi (TGA, Perkin Elmer, STA7200) at healing rate of 10°C/min from 25°C up to 1000°C and in a nitrogen atmosphere. Derivative thermogravimetry DTG curves of these samples were analyzed for obtaining a quantitative estimation of various hydration products such as C-S-H, $Ca(OH)_2$ and $CaCO_3$.

4.3 Results and Discussion:

The results for each round are shown below.

4.3.1 First Round

In the first round, CTAB was the only used surfactant. The primary tests for 28 days of hydration were conducted seeking to optimize the concentration of the components (MWCNT, MCC, and CTAB) for the novel multi-scale MCC-MWCNT cementitious composite and to study their influences on the properties of cementitious composites.

4.3.1.1 Workability:

The values of the average flow of the composites fresh mortar are shown in Table 4-3-. It is apparent that the addition of the MCC, MWCNT and the CTAB did not affect the core workability of the cementitious paste, as all the samples showed relatively good consistency values. Figure 4-3 shows comparison among the different values with the plain mortar value. All the concentrations are with respect to cement unless else written.

Sample	**average flow (cm)**
0.2% MCC+ 0.1% MWCNT+ CTAB (40%MCC+100% MWCNT) + TBP (50% w.r.t CTAB)	18.75
0.5% MCC+ 0.1% MWCNT+ CTAB (40%MCC+100% MWCNT) + TBP (50% w.r.t CTAB)	19.25
0.2% MCC+0.3% MWCNT+CTAB (20%MCC+100% MWCNT) +TBP (50% w.r.t CTAB)	20
0.5%MCC+0.3% MWCNT+CTAB (20%MCC+100% MWCNT) +TBP (50% w.r.t CTAB)	19
0.75%MCC+0.1% MWCNT+CTAB (40%MCC+100% MWCNT) +TBP (50% w.r.t CTAB)	18.5
0.75%MCC+0.3% MWCNT+CTAB (20%MCC+100% MWCNT) +TBP (50% w.r.t CTAB)	19
Plain cement mortar	18.8

Table 4-3 The flow values for plain/MCC-MWCNT reinforced fresh mortars, first round.

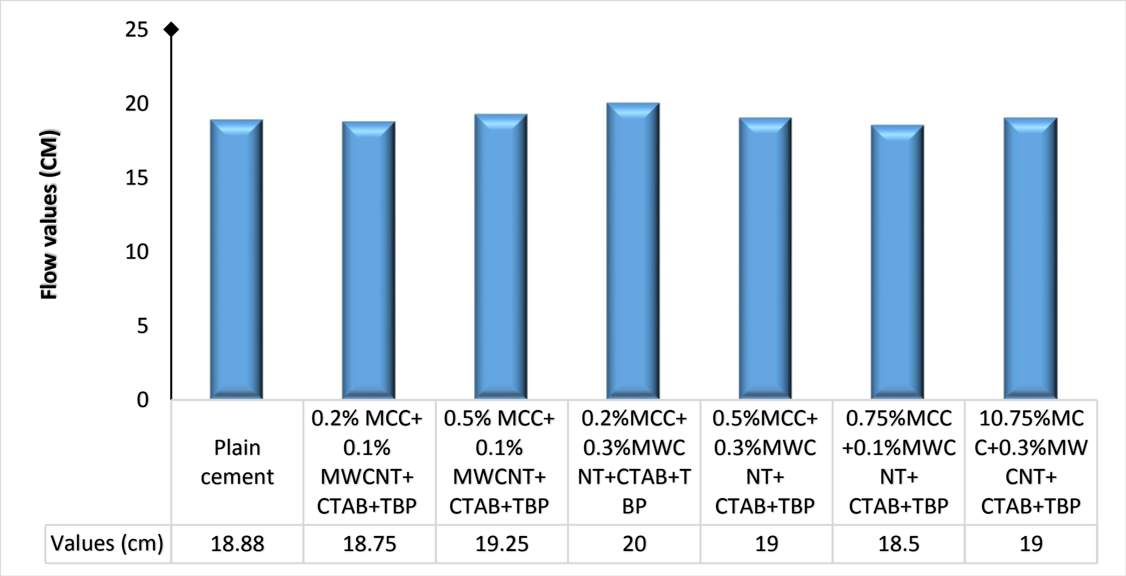

Figure 4-3 Comparison of flow values of MCC-MWCNT reinforced cementitious composite samples/plain mortar, first round.

As it can be noticed, there were no significant changes in the flow values of the composites with the increased concentration of MCC/MWCNT in the composites.

4.3.1.2 Flexural Strength

For the first round, the flexural test was performed to obtain the flexural stress-strain diagrams. Those diagrams are for the MCC-MWCNT samples for the period of 28 days as preliminary results to identify the main flexural properties of the new composites. The Figure 4-4 shows the MCC-MWCNT curves with plain mortar as a reference.

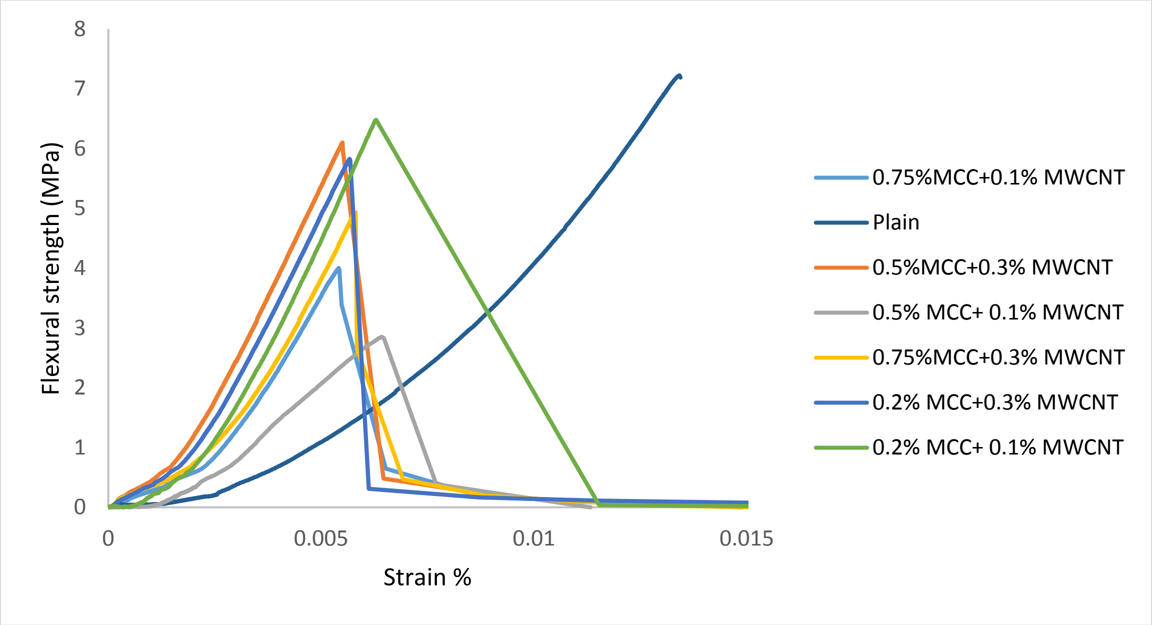

Figure 4-4 Flexural strength results for MCC-MWCNT reinforced cementitious composite and plain mortar, 28 days first round

As it is shown in the previous graph, some of the samples gave better results than others. Clearly the 0.2% MCC + 0.1% MWCNT samples had the best results in terms of flexural strength as well as the strain value while 0.5% MCC + 0.1% MWCN and 0.75% MCC + MWCNT samples proved to be the worst samples of flexural strength, however, it holds good strain values like the best sample. Nevertheless, we can notice that all samples are still lacking flexural strength compared to the plain cement mortar sample. This could be explained by the fact that MCC and MWCNT concentrations needed to be optimized following the condition of cement, as well as the surfactant concentration and TBP. In the case of increased concentration of CTAB without a proportional increase in the TBP, it could affect the composites negatively creating pores that influence the flexural behavior of the composite.

4.3.1.3 Compressive Strength

The values of the compressive strength for MCC-MWCNT composites samples are graphically presented in Figure 4-5 with the plain mortar values as reference.

The compressive strength is linked to many parameters that dominate its characteristics. Expectedly, the 0.2% MCC + 0.1% MWCNT samples showed the best values for the compressive strength compared to the rest of samples and subsequently, the 0.5% MCC + 0.1% MWCNT samples gave the lowest compressive strength. Similarly, all samples showed a significant decrease in the compressive strength as most of them did not achieve 50% of the plain cement strength. Similar to the flexural behavior, the compressive behavior of the composites was generally lower than the plain cement.

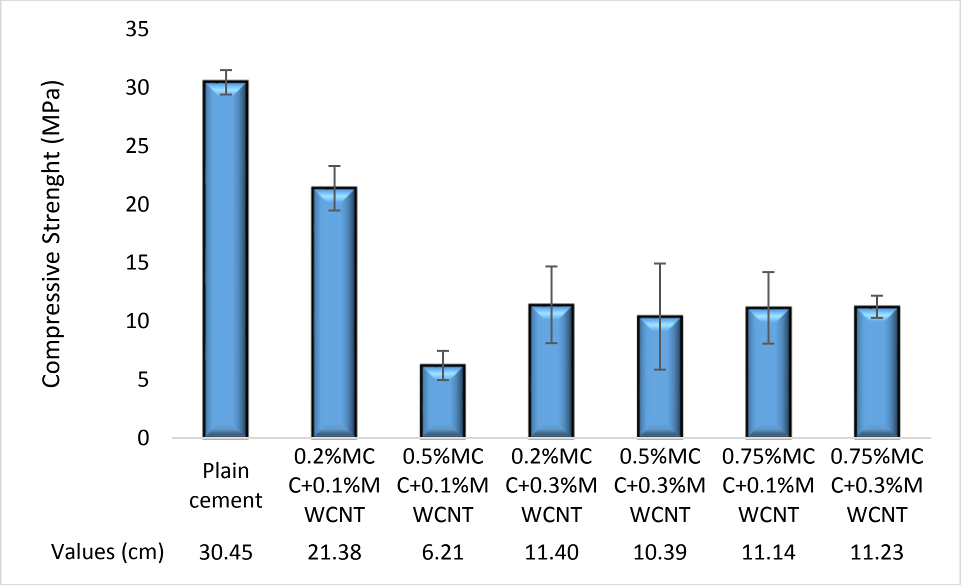

Figure 4-5 Compressive strength results for MCC-MWCNTreinfrced cementitous composites/plain mortar, 28 days first round.

4.3.2 Second Round

The first-round results introduced important information to understand the optimum concentrations of the MCC, MWCNT, and CTAB in the cementitious composite. The samples overall performance was negative, decreased in the mechanical properties were observed due to the unoptimized concentration of defoamer (TBP) with respect to CTAB concentrations. However, the workability evidently was not affected with the addition of MCC, or MWCNT basically.

The main explanations for the drawbacks of first-round samples are; The concentrations of the surfactant and the defoamer needed to be revised in order to obtain better results. It was seen in the broken samples that there were some aggregations of MCC-MWCNTs. It was concluded that the samples should be kept in mechanical stirring till the final addition in the cement inside the Hobart mixer to ensure that there were few or no agglomerates of MWCNT/MCC.

Thus, the second round was performed with optimized concentrations of MCC, MWCNT, defoamer and surfactant. Two kinds of surfactants were considered. The surfactant Pluronic F-127 was utilized in comparison with the CTAB. The Pluronic F-127 proved to have a good influence on the MWCNT cementitious composites. In this round, two sets of samples were produced to accomplish two periods of hydration: 28 and 56 days, for the sake of better and more definite understanding of the new composites. Similarly, the tests on the second round were more extensive, detailed and collective.

4.3.2.1 Workability:

The flow values of the second-round samples are presented in Table 4-4. Equally to the first round, the MCC and MWCNT particles did not affect the consistency of the new composites. The workability values are good compared to the plain mortar samples.
Figure 4-6 shows comparison among the different values with the plain mortar value. All concentrations are with respect to cement unless different written.

Sample name	**Left (mm)**	**Right (mm)**	**Average Flow (mm)**
Plain Cement	189	187	188
0.2% MCC+0.1% MWCNT+ CTAB+0.75 TBP	170	172	171
0.2% MCC+0.1% MWCNT+ CTAB+1 TBP	185	190	187.5
0.5% MCC+0.3% MWCNT+ CTAB+0.75 TBP	220	215	217.5
0.5% MCC+0.3% MWCNT+ CTAB+1 TBP	200	195	197.5
0.2%MCC + 0.1%CNT + TPB + 1.5%P	195	200	197.5
0.5%MCC + 0.3%CNT + TPB + 1.5% P	200	195	197.5

Table 4-4 The flow values for plain/MCC-MWCNT reinforced fresh mortars second round.

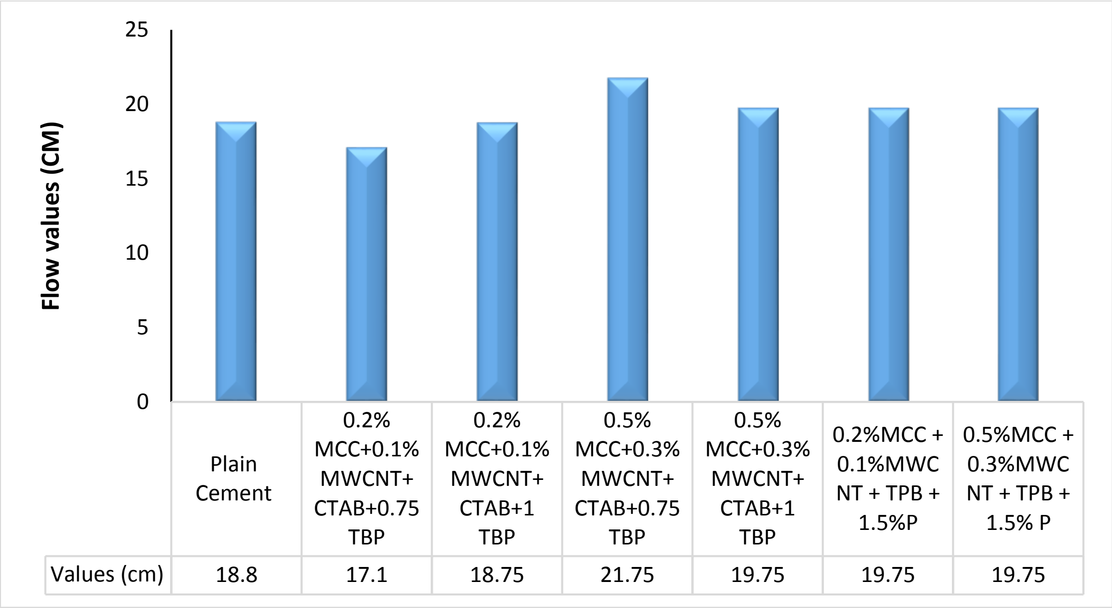

Figure 4-6 Comparison of flow values of MCC-MWCNT reinforced cementitious composite samples/plain mortar, second round.

4.3.2.2 Flexural Strength

In the second round, promising results were obtained. The flexural tests were done for MCC-MWCNT samples for periods of 28 days and 56 days respectively. In Figure 4-7 the results of the 28 day curves are presented with the 28-day plain mortar as a reference

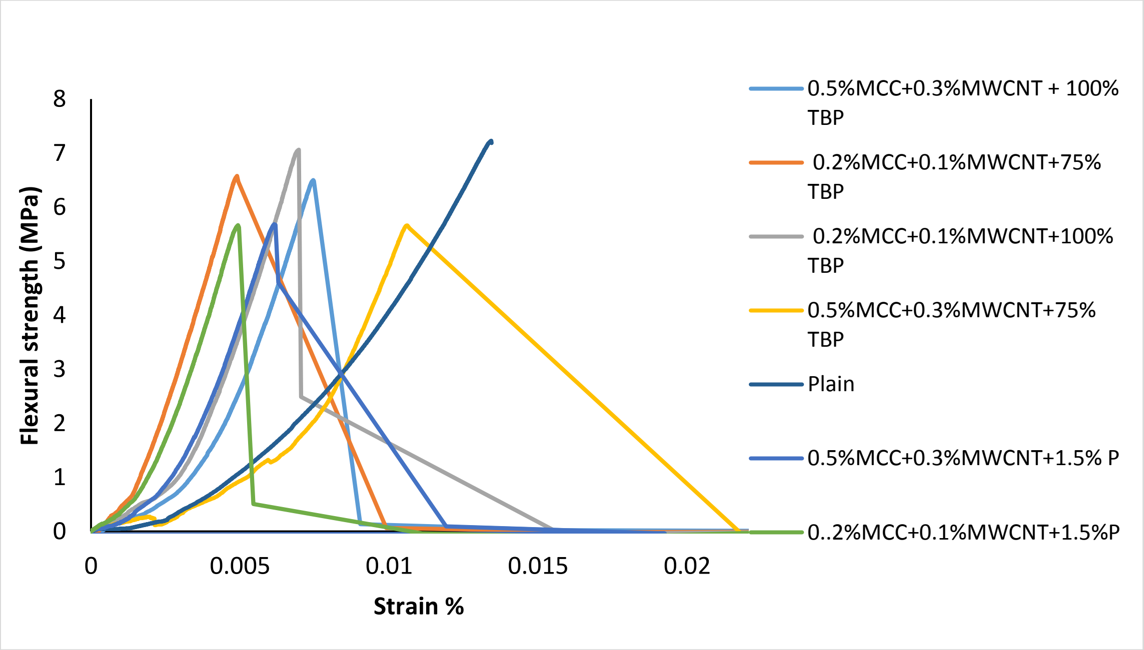

Figure 4-7 Flexural strength results for MCC-MWCNT reinforced cementitious composite and plain mortar, 28 days second round

Clearly, in the second-round, higher results were achieved due to the optimization of the concentrations and the accuracy of the performed samples. In this round, all the samples achieved higher results compared to the first round, with 0.2%MCC + 0.1%MWCNT + 100%TBP + CTAB reaching almost the plain cement peak, followed by the 0.5%MCC + 0.3%MWCNT + 100%TBP + CTAB samples.

The results of the 56 day curves are presented with the 56-day plain mortar samples as a reference in Figure 4-8. Interesting results were achieved in 56day curves, with Pluronic F-127 samples as 0.2%MCC + 0.1%MWCNT + 1.5%P samples had the peak of the curves and reached higher strength compared to the plain mortar with an improvement of approximately 14%. Parallel results were reached with the 0.5%MCC + 0.3%MWCNT + 100%TBP + CTAB samples as they surpassed the plain mortar sample with up to 13% improvement rate.

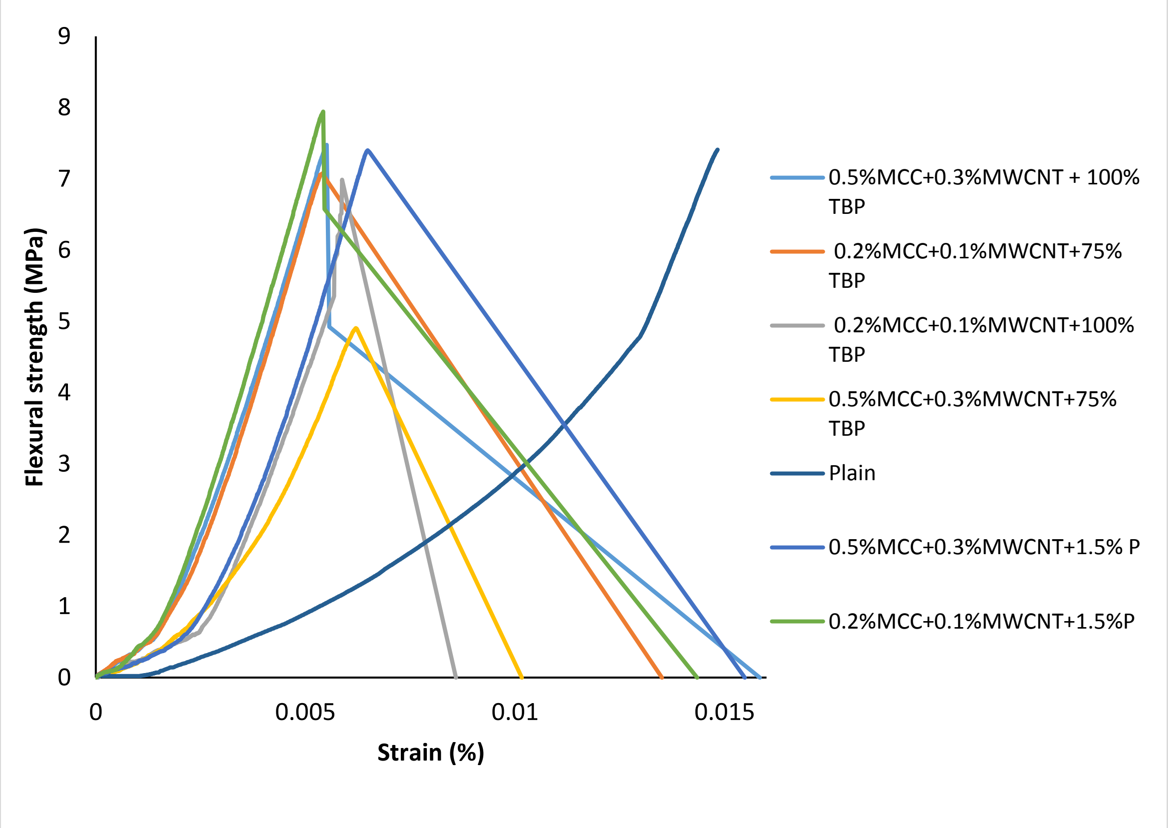

Figure 4-8 Flexural strength results for MCC-MWCNT reinforced cementitious composite and plain mortar, 56 days second round

4.3.2.3 Compressive Strength

The average compressive strength results for 28 and 56 days, second round samples, are presented in Table 4-5.

Sample name	Average compression strength 28 days (MPa)	Average compression strength 56 days (MPa)
Plain Cement	30.45 ± 1.04	32.09 ± 1.43
0.2% MCC+0.1% MWCNT+ CTAB+0.75 TBP	25.43 ± 7.91	40.44 ± 3.87
0.2% MCC+0.1% MWCNT+ CTAB+1 TBP	35.14 ± 3.52	35.58 ± 0.73
0.5% MCC+0.3% MWCNT+ CTAB+0.75 TBP	19.35 ± 2.07	24.61 ± 1.87
0.5% MCC+0.3% MWCNT+ CTAB+1 TBP	35.4 ± 3.15	39.05 ± 6.64
0.2%MCC + 0.1%MWCNT + TPB + 1.5%P	27.95 ± 3.75	36.42 ± 2.21
0.5%MCC + 0.3%MWCNT + TPB + 1.5% P	21.61 ± 2.83	29.04 ± 4.18

Table 4-5 Compressive strength results for 28/56 day samples round two. *± values are the 95% confidence intervals calculated from the modulus and strength data.

As can be seen in Figure 4-9, the values of the 28 day samples were superior to ones of the first-round samples generally with 0.2%MCC + 0.1%MWCNT + CTAB + TBP and 0.5%MCC + 0.3%MWCNT + CTAB + 1TBP samples achieving higher results than the plain cement ones in the 28 days, with 15% and 16% improvements. Also, the 56 day samples had enhanced and more improved strength and that is reasonable as the hydration process influence the compressive strength of the sample positively. With approximately 26% and 21% for the same CTAB samples exceeded the plain cement ones after 56 days of hydration. While the 0.2%MCC + 0.1%MWCNT + TPB + 1.5%P samples had a 13% higher strength compared to the plain cement after the same period.

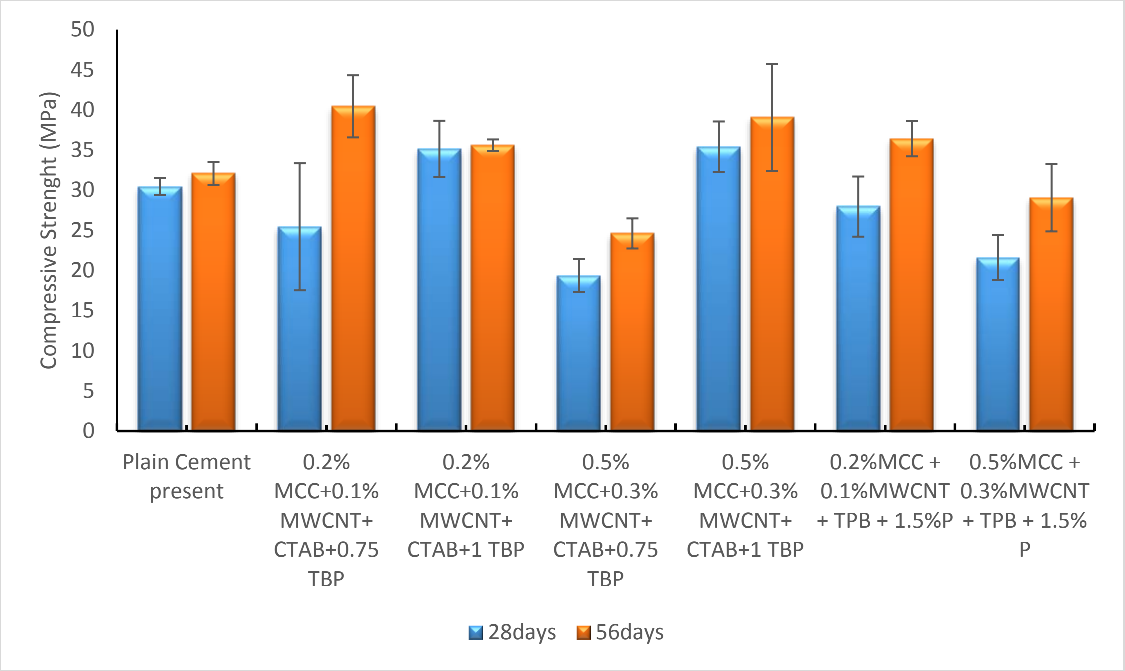

Figure 4-9 Comparison of compressive strength results for MCC-MWCNT reinforced cementitious composites/plain mortar, 28 and 56 days second round.

4.3.2.4 Mercury Intrusion Porosimetry (MIP):

The results of the MIP analysis were conducted for the best samples to better understand the initial properties in terms of porosity. The main results of each sample porosity and average pore diameter are presented in Table 4-6. more detailing, the curves demonstration the relations between incremental Intrusion and pore size diameter for each sample are presented in Figure 4-10 and Figure 4-11.

28 days	Porosity %	Average pore diameter
Plain Cement	10.50%	47.4nm
0.5% MCC+0.3% MWCNT+ CTAB+0.75 TBP	17.40%	41nm
0.5% MCC+0.3% MWCNT+ CTAB+1 TBP	12.97%	30nm
0.2%MCC + 0.1%MWCNT + TPB + 1.5%P	13.9504	28nm
0.5%MCC + 0.3%MWCNT + TPB + 1.5% P	15.31%	33.9nm

Table 4-6 the porosity percentage and average pore diameter for best samples of MCC-MWCNT reinforced cementitious composites and plain cement, second round.

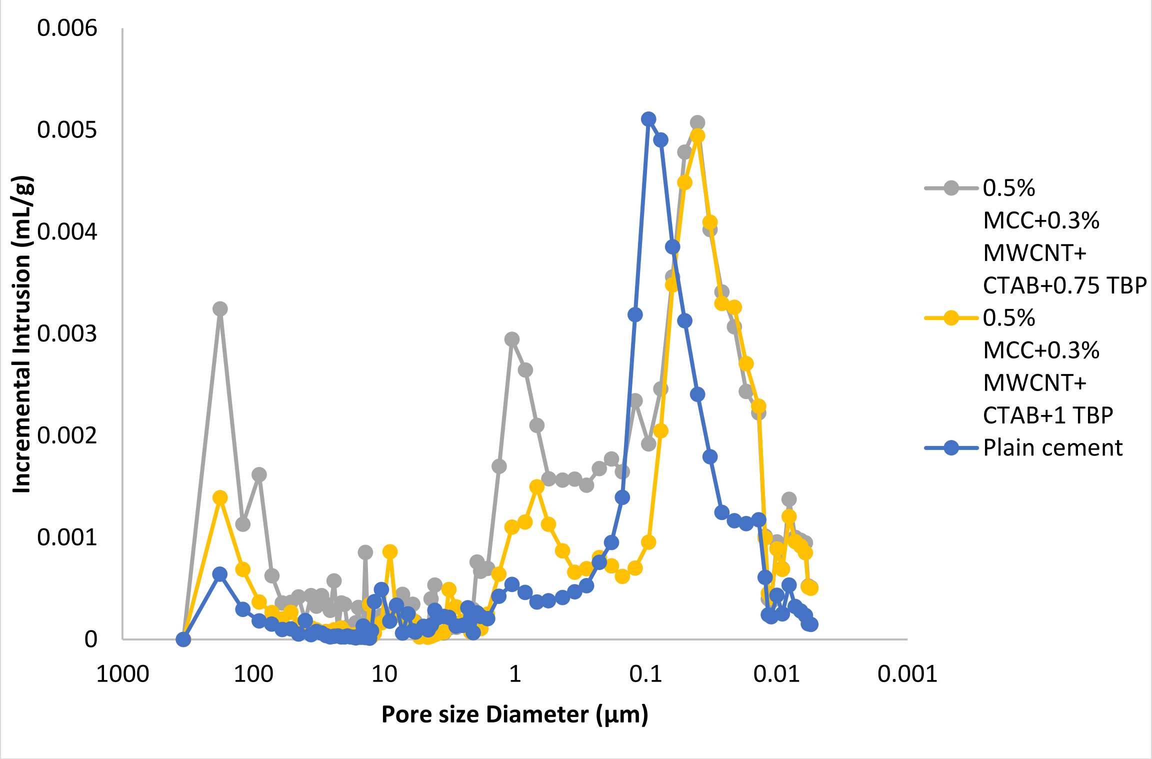

Figure 4-10 The incremental intrusion/pore size diameter curves for plain cement /MCC-MWCNT reinforced cementitious composites samples dispersed using CTAB.

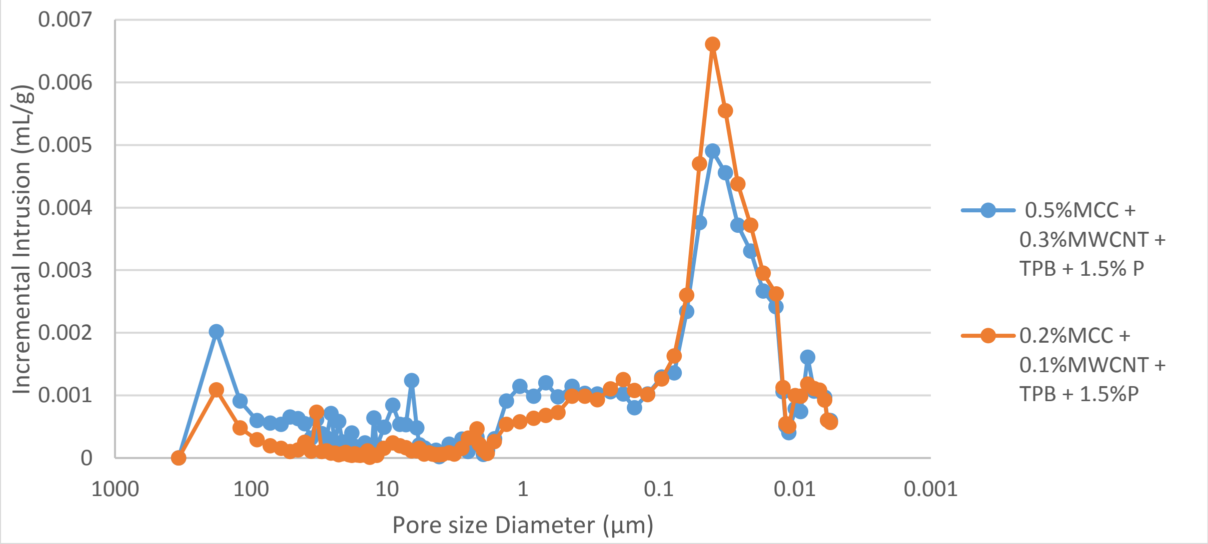

Figure 4-11 The incremental intrusion/pore size diameter curves for MCC-MWCNT reinforced cementitious composites samples dispersed using Pluronic F-127.

In Table 4-6, a close attention should be paid to the pore diameter and not only to the porosity percentage. Both CTAB and Pluronic F-127 samples achieved good results regarding pores diameter, as in 0.5% MCC + 0.3% MWCNT + CTAB + 1 TBP and 0.2%MCC + 0.1%MWCNT + TPB + 1.5%P having the best values of 30 nm and 28 nm, respectively. The largest porosity in the new composites was reached with 0.5% MCC + 0.3% MWCNT + CTAB + 0.75 TBP sample with only 41 nm for average pore diameter which is still lower than the plain mortar sample of 47.4 nm average pore diameter.

As shown in Figure 4.3.2.4-b, the peak intrusion was for the pores with diameter of around 40nm for both 0.5% MCC + 0.3% MWCNT + CTAB + 0.75 TBP and 0.5% MCC + 0.3% MWCNT + CTAB + 1 TBP samples. And this good characteristic is shared clearly in 0.2%MCC + 0.1%MWCNT + TPB + 1.5%P and 0.5%MCC + 0.3%MWCNT + TPB + 1.5% P samples with a highest intrusion for pore diameter of 40.3nm as plotted in figure. In contrast, the plain cement samples had a peak intrusion with a relatively large pore diameter around 95nm. This implies that the diameter of the pores for peak intrusion was significantly reduced with the new composites nearing the average pores diameter in the samples.

The MWCNT and MCC particles create some agglomerations, those agglomerations affect the overall porosity percentages, however, the average pore diameter is decreased due to the structure of the particles themselves. Thus, the overall porosity percentages are slightly higher in the new composites compared to the plain mortar while the diameter of the pores is lower [57].

4.3.2.5 Dry Bulk Density

The results of the dry bulk density for the samples 0.2%MCC + 0.1%MWCNT + 1 TBP + 1.5%P, 0.5%MCC + 0.3%MWCNT + TBP + CTAB which represents the best samples in the MIP analysis, are presented in Figure 4-11, with plain cement sample as a reference.

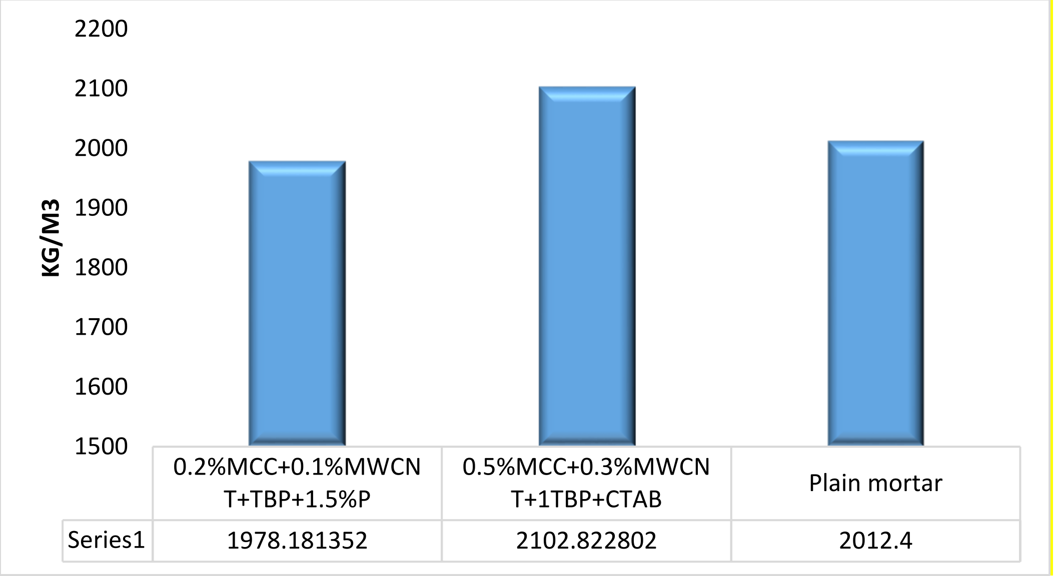

Figure 4-12 Dry bulk density results for Plain and MCC-MWCNT reinforced cementitious composites

Both new MCC-MWCNT cementitious composites have relatively a close bulk density to the plain mortar. That is substantial as both samples scored similar porosity percentage and were the lowest overall and the closest to the plain mortar porosity percentage.

In the first Pluronic F-127 samples, the overall bulk density was reduced creating a less dense sample, that could be explained with the idea of the new configuration of MCC and MWCNT as their dispersion could affect the sample microstructure after reacting with Pluronic F-127 and create more pores, enlarging the overall volume of the sample. The second sample with the CTAB had a negligible higher density making the sample marginally denser. This is due to the conditions that happen occasionally when CTAB well-dispersed samples affect the structure of the compound. In our case, the CTAB helped to disperse the cement particles that possess the size particles of 22-50 μm. Thus, we achieved better density properties.

4.3.2.6 TGA Analysis

The TGA analysis results are presented in Figure. 4-14. The derivative weight loss for plain cement mortar, as well as the samples 0.2%MCC + 0.1%MWCNT + TBP + 1.5%P and 0.5%MCC + 0.3%MWCNT + TBP + CTAB, are plotted with the three curves showing the relation of weight loss along with the temperature raising. The evaporation of free water or the water on the CSH surface is represented by the first peak (around 100° C). The second peak represents the decomposition of $Ca(OH)_2$. The third and last peak is related to the existing amount of $CaCO_3$ in the sample.

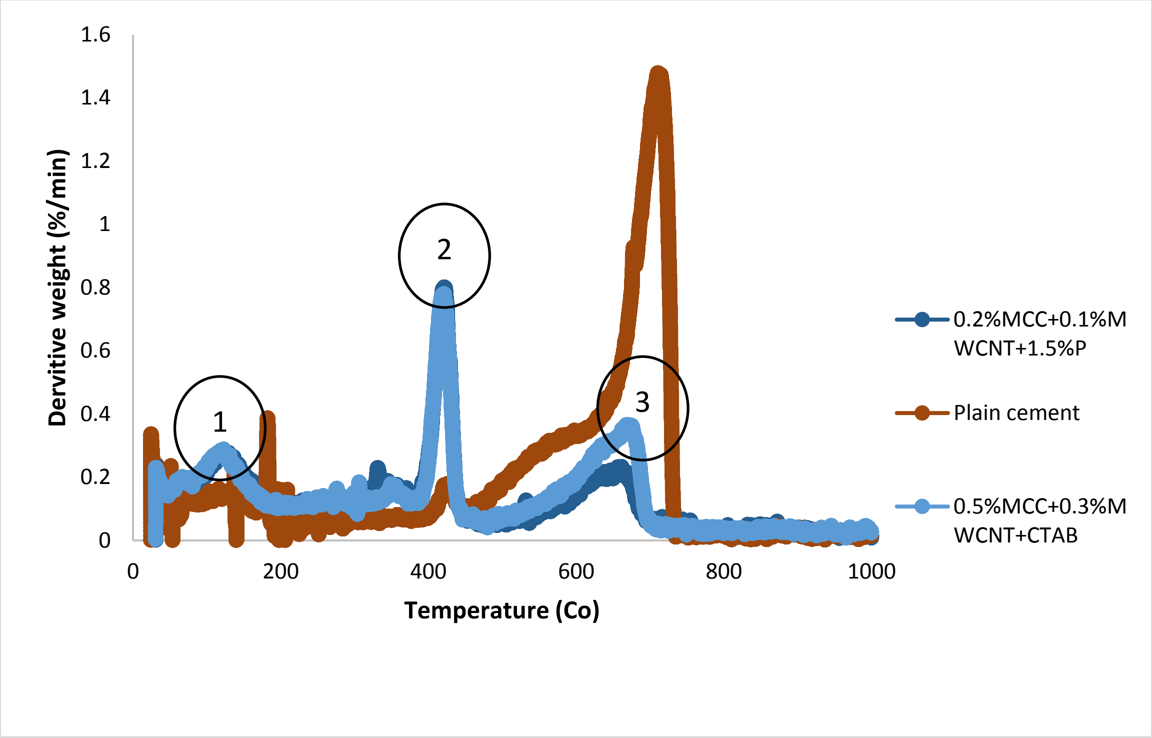

Figure 4-13 Derivative weight loss curves for plain cement mortar and MCC-MWCNT reinforced cementitious composites

As it can be seen in the new composites of MCC-MWCNT with either Pluronic F-127 and CTAB, second peaks have higher intensity compared to the plain cement one. This could be explained as the formation of CSH gel and $Ca(OH)_2$ was higher in the case of MCC-MWCNT composites. Due to MCC water retention ability, it can release water to speed the hydration process. The third peak represents usually microstructure of the sample, as we can see less amount of CaCo3 was present in the case of MCC-MWCNT composites, which with considering the hydration degree implies less density in case of plain mortar. As hydration products fill up spaces while developing. That fits well with the Bulk Dry Density results as we saw at the microstructure level that MCC-MWCNT composites particles are more compressed and well dispersed compared to the plain mortar ones, although the higher porosity percentage.

4.4 Conclusions

In this Chapter 4 MCC-MWCNT suspensions mentioned in Chapter 3 were used to produce the new cementitious composites. The influence of the MCC-MWCNT concentration, type and concentration of the surfactant, the combined dispersion technique and the hydration period on the main properties of the new composites were investigated in details to acquire a better understanding. The following conclusions could be drawn from this work:

1- MWCNTs and MCCs have high-quality dispersion utilizing CTAB or Pluronic F-127, however, they need significantly higher concentration with Pluronic F-127 (1.5% w.r.t cement) compared to the CTAB (0.2-0.6% w.r.t cement)
2- MWCNT and MCC were noticed to have agglomeration when above 0.3% of MWCNT w.r.t cement while lower concentrations showed slight or no agglomerations.
3- MWCNT and MCC showed good flexural and compressive properties when reinforced with 0.5%MCC and 0.3% MWCNT when dispersed using CTAB. While both 0.2% and 0.5% MCC with 0.3% and 0.1% MWCNT samples had high strengths when dispersed with 1.5% of Pluronic F-127 w.r.t. cement.
4- the optimized concentration of defoamer TBP with CTAB sample gave improved mechanical properties for the cementitious composites due to the voids mitigation.

5- The workability of the cementitious paste was trivially not affected by the MCC and MWCNT dispersed with both surfactants. The addition of MCC and MWCNT using either CTAB or Pluronic F-127 did not significantly influence the workability of mortar paste.
6- Significant enhancements in flexural strength were achieved with a higher concentration of MCC (0.5%) and MWCNT (0.3%) in the case of both CTAB (14%) and Pluronic F-127 (13%).
7- The overall ductility of the composites was improved in almost all the MCC-MWCNT samples as the breaking strain increased. However, the stiffness experienced slight or no changes and was not increased in most of the samples.
8- A maximum improvement in compressive strength of approximately 26% was obtained with 0.2% MCC and 0.1% MWCNT with both CTAB and Pluronic F-127 which is followed by 0.5%MCC 0.3% MWCNT samples dispersed using CTAB and TBP.
9- The bulk density has slight fluctuation in the case of both Pluronic F-127 and CTAB sample with denser mortar in the case of Pluronic F-127.
10- The overall porosity of the samples improved with smaller average pore diameter in most of the samples, leading to a denser microstructure in comparison with the plain mortar.

Chapter 5

Conclusions and Future Work

5.1 Conclusion

The nanotechnology has high promises for the construction industry. More sustainable and stronger materials are sought. Concrete itself is responsible for more than 10% of all industrial CO_2 emission worldwide. To improve the mechanical properties and the microstructure of the cementitious composite with more environment-friendly materials, this research was conducted.

The main objective of this thesis is to study the novel approach of multiscale incorporating of MCC and MWCNT particles in the cementitious composites. The main results provided a better understanding of the MCC-MWCNT influence on the cement based materials. The experiments were on two round using a combined dispersion technique with two different types of surfactants used. CTAB was used solely in the first round of the work to study the optimum concentration of all component. Pluronic F-127 and CTAB were used in the second round and the final influences on the mechanical and microstructure properties of the new composites were studied in details.

The main results that are concluded from this work are briefly presented below:

1- The integration of both materials on a multiscale level could be efficacious with a thorough study of both materials properties.
2- The new MCC-MWCNT composite can positively enhance the building sustainable properties. The MCCs and MWCNTs enhance the cementitious composite overall properties by adding a small amount of them. This could alternate a large amount of ordinary cement leading to more sustainable construction.
3- The various optimal concentration of MCC up to 0.5% w.r.t water and MWCNT up to 0.3% could successfully be dispersed to produce a homogenous suspension, following an unconventional technique consists of physical and chemical dispersion methods.
4- Stable suspensions of MCC and MWCNT were prepared by using either Pluronic or CTAB as a chemical method and following it with mechanical stirring for short time and ultrasonication for 30 minutes in medium energy 80W as physical techniques.
5- Both surfactants proved positive in improving the mechanical properties at different levels, however, Pluronic needed relatively higher concentrations (up to 10 times more than CTAB) to perform well.

6- MCCs and MWCNTs composites achieved good mechanical properties, by maintaining the workability, enhancing the porosity status, increasing the ductility because of the MWCNT, improving the compressive strength with 26% in case of 0.2%MCC + 0.1%MWCNT + CTAB + TBP and up to 13% improvement with 0.2%MCC + 0.1%MWCNT + TPB + 1.5%P samples, and importantly improving the flexural strength around 14% with both 0.2%MCC + 0.1%MWCNT + 1.5%P and 0.5%MCC + 0.3%MWCNT + 100%TBP + CTAB samples after 56 days of hydration.

5.2 Future Works

The nanotechnology is increasingly gaining prominence in the construction industry. So, this multiscale incorporation of MCC and MWCN seems a promising area of study and the development of this composite could lead to a commercial version in the future. The possible suggestions for the development of this research could be summarized as follow:

- Development of the MCC-MWCNT composites with the optimum concentration to study the overall electrical behavior of the composite as carbon nanotubes cementitious materials are also piezoresistive.
- A thorough investigation of the influence of Tributyl Phosphate (TBP)on the cementitious composite should be done in order to understand the dispersion capabilities of TBP.
- Investigations should be made to study the effect of various parameters of dispersion of MWCNTs on the interphase of MWCNTs and cement matrix.
- Development and study for the possible recyclability of the composite and conducting a full life cycle analysis should be done in a proper manner.

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Annex 1

Publications in International Conferences

1- Ahmad Alshaghel, Shama Parveen, Sohel Rana, Raul Fangueiro, "Mechanical properties of carbon nanotube–microcrystalline cellulose reinforced multi-scale cementitious composites", accepted as oral, ICNF2017, Braga, Portugal, 21-23 June.

2- Ahmad Alshaghel, Shama Parveen, Sohel Rana, Raul Fangueiro, "New multi-scale cementitious composites developed using carbon nanotubes and microcrystalline cellulose", oral presentation, MATERIAIS 2017 Aveiro, Portugal, 9 – 12 April.