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[UCI]I804:24011-200000266263

August 2017

Master's Degree Thesis

Experimental investigation on the shrinkage and hydration kinetics of cement paste matrix incorporated with MWCNT

Graduate school of Chosun University

Department of Architectural Engineering

Major: Building and Material Engineering

Million Tafesse Bedso

조선대학교
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Experimental investigation on the shrinkage and hydration kinetics of cement paste matrix incorporated with MWCNT

MWCNT 혼입 시멘트 페이스트의 수축과 수화성상변화에 대한 실험적 연구

August 25, 2017

Graduate School of Chosun University

Department of Architectural Engineering

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Experimental investigation on the shrinkage and hydration kinetics of cement paste matrix incorporated with MWCNT

Advisor: Professor Hyeong-Ki Kim

This thesis is submitted to graduate School of Chosun University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Architectural Engineering

April, 2017

Graduate School of Chosun University

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Major: Building and Material Engineering

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May, 2017

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Abstract

Experimental investigation on the shrinkage and hydration kinetics of cement paste matrix incorporated with MWCNT

Million Tafesse, Bedso, B.Sc

Advisor: Prof. Hyeong-Ki Kim, Ph.D.

Department of Architectural Engineering

Graduate school of Chosun University

In this Research, a detailed study is done aiming to investigate the effect of the nano-filament, Multiwalled Carbon Nanotube (MWCNT), on the hydration kinetics, shrinkage and engineering properties of a cement paste matrix incorporated with MWCNT. Micro-level silica fumes were used to disperse the CNT mechanically throughout the cement matrix with a low water-binder ratio. The research was performed in two basic parts; one is analyzing the effect of the CNT on the engineering property of the cement paste matrix such as flowability, compressive strength, flexural strength, and dynamic modulus. The other is investigating the CNT effect on the shrinkage and hydration kinetics by analyzing data's from, linear deformation, isothermal calorimeter, and degree of hydration measurement. In general, from the experimental result except for the compressive strength, the flexural strength and dynamic modulus of elasticity show an increase by incorporating CNT in the cement matrix. However, the addition of CNT led an increase in dry and autogenous shrinkages but the degree of hydration was not changed by the use of CNT.

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Abstract in Korean

MWCNT 혼입 시멘트 페이스트의 수축과 수화성상변화에 대한 실험적 연구

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Department of Architectural Engineering

Graduate School of Chosun University

시멘트 페이스트 매트릭스의 수화 속도, 수축 및 엔지니어링 특성에 대한 Multiwalled carbon nanotube (MWCNT) 의 효과를 조사하기 위한 연구가 수행되었다. CNT 를 시멘트 매트릭스 전체에 고르게 분산시키기 위해 실리카퓸과낮은 물 바인더 비율이 적용되었다. 이 연구는 두 가지 부분으로 구성되었다. 먼저 유동성, 압축 강도, 굴곡 강도 및 동적 계수와 같은 시멘트 페이스트 매트릭스의 공학적 특성에 대한 CNT 의 영향을 분석하는 것이다. 이후수축, 미소 수화열 및 수화도를측정 분석하여 수축 및 수화 속도에 CNT 효과를 조사하는 것입니다. 일반적으로 압축 강도를 제외한 휨강도와동탄성계수는 시멘트 기지 내에 CNT 를 혼입시킴으로써 현저한 증가를 보였다. 그러나, CNT 는 일부 수축량을시키고 수화율을 낮추었다.

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Dedication

This thesis is dedicated to the Virgin Mary, Holy Mother of God and for the Angels of God.

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Chapter 1. Introduction

1.1 Background

The need to change, shape, and innovate a material in our surrounding has come to a new level due to a microscopic scale study of material properties. One of the basic concepts of Nanotechnology in the physical science level is bottom-up engineering, which means adjusting materials at a molecular level to shape the overall property of a material (TRB, 2012). Even though, nanotechnology is recently developing in the construction sector there are some advancements in the use of the technology. Advancements such as, to improve mechanical properties, to shape materials with a self-cleaning ability, to give materials an electron conductive capability and to influence cement hydration products (NMP, 2013; Logothetidis, 2012; Zhu et al., 2004).

In the case of this research project, one of the nanomaterials, MWCNT, is used to incorporate it in the cement paste matrix. MWCNT was used for this research because of its high, mechanical strength, thermal conductivity, and chemical stability; moreover, the higher aspect ratio and surface area give MWCNT particles the ability to reinforce cement matrix as a fiber (WU, 2009). In addition, it will increase the flexural strength and toughness of the cement composite (Kim, 2014). Even though there are plenty of researches on MWCNT effect on the mechanical property of cement composite, however, there are limited studies on explaining the effects on hydration kinetics and linear deformation. This research tries to fill the knowledge gap by experimentally investigating the effects in detail, and this study is a novel study of its kind. In general, the objective of this paper is to study the mechanical

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properties, shrinkage and hydration kinetics of the cement paste matrix reinforced by Multi-welled Carbon Nanotube (MWCNT) fiber.

1.2 Procedure of the thesis

This study in general covers the properties of MWCNT incorporated in a cement matrix by investigating the capability and role on the mechanical strength, shrinkage, and degree of hydration. The thesis is composed of five chapters. The layout is shown in a flowchart in Figure 1.1.

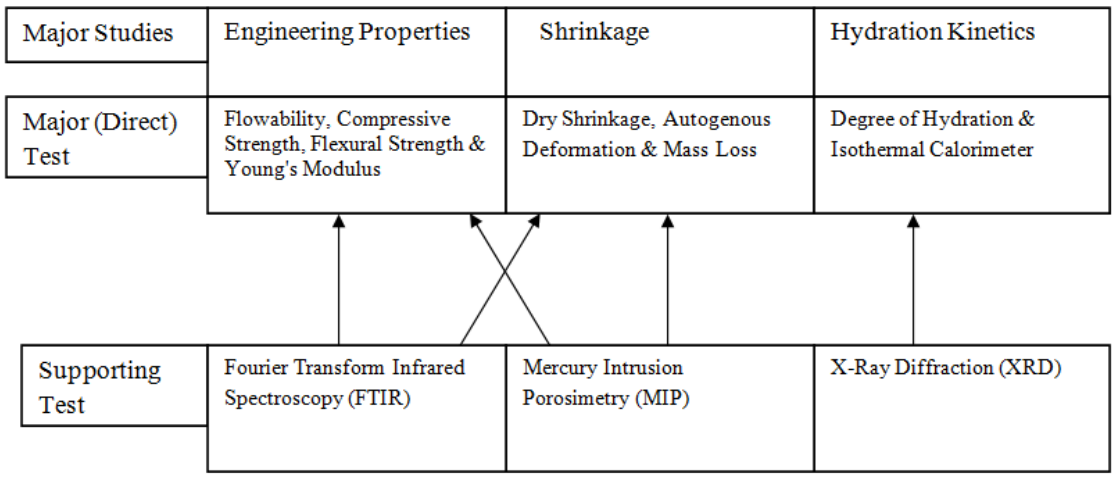

Figure 1.1 Lay out of this thesis

Chapter one of this thesis discusses the outline and main aim of the study in a short and brief description.

Chapter two of this thesis introduces the main theoretical background for the thesis as a literature review to lay a foundation for the further discussion on next chapters. In this chapter,

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an introduction to previous works in the area will be discussed followed by a detailed introduction to the two main components of the study, CNT, and Silica fume, describing their properties in the cement paste matrix. Besides, an introduction to the terminology and mechanism of shrinkage and degree of hydration is made with a final concluding remark of the chapter.

Chapter three of this thesis discusses the effect of MWCNT on the cement paste matrix engineering properties and these results has been used as a background data for the effects on the shrinkage and hydration kinetics study. Before the investigation, the functional group and the absorbance intensity of the MWCNT with water and carboxylic-based superplasticizer were analyzed. Some of the engineering properties assessed in this study are flowability, compressive strength, flexural strength and dynamic young's modulus. In the last part of the chapter, engineering property conclusions have been made based on the results.

Chapter four of this thesis, in general, investigates the MWCNT effect on shrinkage and degree of hydration. In addition, the methods used to study both the shrinkage and hydration kinetics are explained briefly including the procedures used during the assessment with a detailed discussion on the results. Finally, a conclusion is made based on the results and previous studies.

Chapter five of this thesis is a complete summary of the core points in the thesis including the limitations and future research plans.

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1.3 Objective of the thesis

The main aim of this study is to investigate:-

- the engineering properties of the MWCNT incorporated in cement paste matrix.
- the shrinkage and hydration kinetics of cement paste incorporated with a MWCNT.
- the interaction between the MWCNT and the hydration products of cement composite materials.

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Chapter 2. A synopsis on the backgrounds and literature reviews -A review

2.1 Introduction

Nanotechnology is one of the most advanced and contemporary time science fields with an enormous potential for the construction field (Lelusz, 2014; Zhu et al., 2004). A roadmap published back in 2009 shows the general nanotechnology advancement in the construction industry for the future implying its high opportunity in the research field. The roadmap is shown in Figure 2.1 (Bartos, 2006). For the last decade, researchers use different nano-materials for a different purpose in the construction sector to modify building materials. Some of the nanomaterials are, graphene oxide, carbon nanotube, titanium oxide, zinc oxide, aluminum oxide, nano-silica, nano-clay and others in the nanoscale level are being used as a construction material modifications successfully (Sanchez and Sobolev, 2010).

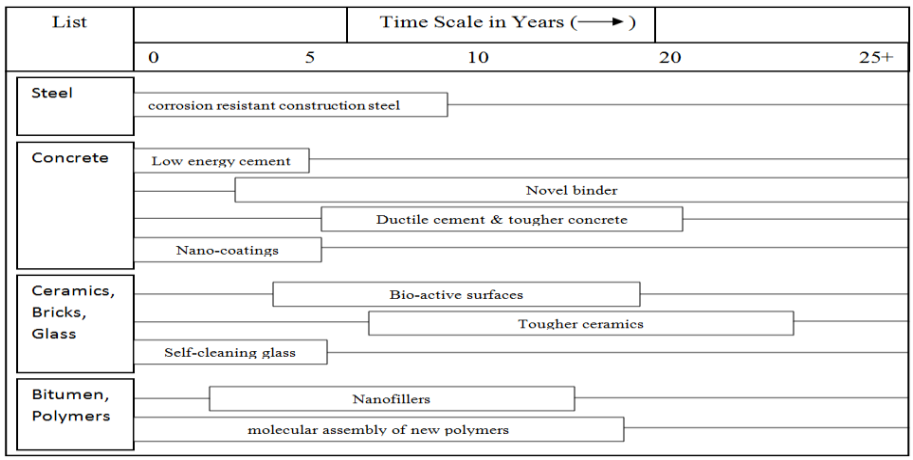

Figure 2.1 Road map for bulk construction materials (Bartos, 2006)

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One of the nanomaterials, carbon nanotube (CNT) is currently attracting many studies due to its astonishing mechanical, electrical (R=5-50μΩcm), chemical (highly stable) and thermal (2800 ℃ for vacuum) property (Bernholc et al., 2002; Ong et al., 2010; Fukuda et al., 2003). The mechanical property of CNT is remarkable, the young's modulus is approximately 0.3-1TPa and has yield strength around 10-60 GPa with an aspect ratio of 10-1000. The aspect ratio gives the CNT a fiber capability to reinforce the hydration products of cement paste at a micro level. Furthermore, CNT increases the tensile strength and the compressive strength. On the other hand, the tendency of CNT to agglomerate easily due to their high van der waals forces caused by the large surface area of CNT requires an appropriate desperation technique (Sanchez, 2009; Gay, 2010; Manzur, 2014). However, many studies claim that most of the desperation techniques have theirs on limitations. For example, most researchers used sonication as a desperation technique. However, some researchers claim that these techniques lead to a creation of air bubbles on the cement matrix weakening the composite structure due to the surfactants used in the sonication process. In addition, it leads to fragmentation of the nanotube itself by reducing the aspect ratio (LU, 1996; Konsta-Gdoutos et al., 2010) and most chemical desperation techniques has an adverse effect on the hydration products weakening the durability. To overcome such problems a silica fume with an extremely fine particle can be intermixed with the CNT to separate the agglomerated CNTs mechanically (Sanchez and Ince, 2009). This research lies on the capability of silica fume to enhance the dispersion of CNT (Kim, 2014; Kim, 2016). The detail characteristics and property of CNT and silica fume are explained in this chapter including the basic definitions and terminologies of shrinkage and hydration kinetics.

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2.2 CNT

CNT is one of the four pure forms of carbon allotrope beside diamond, graphite, and fullerenes. It have a tubular (circular tube shape) structure predominantly containing carbon atoms as shown in the Figure 2.2. Additionally, the carbon-to-carbon covalent bondage interlocking and the fact that each single CNT by itself is a one large molecule having a hexagonal lattice structure give CNT a unique property as shown in Table 2.1.

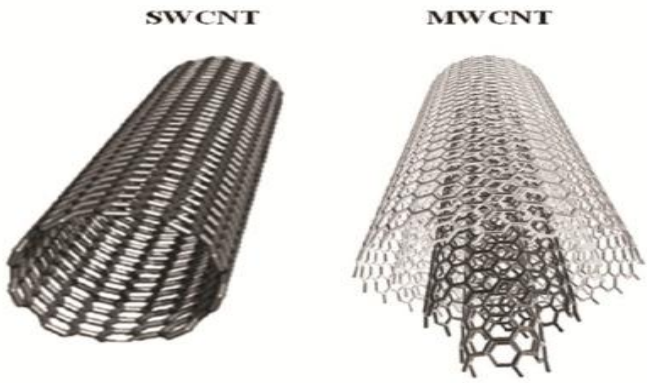

Figure 2.2 Pictures of CNT; SWCNT and MWCNT (www.nanoscience.com)

In general, CNT is classified as Single Walled Carbon Nanotube (SWCNT) and Multi Walled Carbon Nanotube (MWCNT). The main difference between the two types of CNT is that SWCNT is one layer and MWCNT is a concentric circle of the SWCNTs. Ebbesen and Ajayan first did the productions of both, SWCNT and MWCNT in macroscopic scale after one year from SumioIijima discovery of CNT in 1991 (NEC fundamental research laboratory) (Iijima, 1991; Ebbesen and Ajayan,1992).

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Table 2.1 Material property of CNT (Bernholc et al., 2002; Ong et al., 2010; Fukuda et al., 2003)

Diameter (nm)	Length (μm)	Aspect ratio	Purity (%)	Ash wt(%)	Surface area	Density (Kg/m3)	Electric conduct-ivity (s/cm)	Tensile strength (GPa)	Elastic modulus (GPa)	Rupture elongation (%)
10-80	5-15	1000-10000	>95	<3	40-300	1330	(15-30) × 10^{-3}	11-63	1000	12

2.2.1 Production of CNT

Recently there are three well-known techniques for the production of CNT. Even though there are trials for new ways of production but they had less success. Each of the three methods is discussed shortly here.

1. Arc Discharge Method: This is the pioneer method in production of CNT. Uses anode and cathode bars made from mostly pure graphite to pass current between the road bars. While, the current pass through the graphite bar it will vaporize the carbon from the anode and gather it into the Cathode, forming either MWCNT or SWCNT with simple modifications (Borisenko, 2002).

2. Laser Ablation (LA): Technically this method is similar with that of Arc discharge. Uses graphite bars to vaporize the carbon from the anode to the Cathode by a pulsing laser. The CNTs produced by this method have high purity; however, it is expensive due to the cost of laser (Chrzanowska, 2015)

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3. Chemical Vapor Deposition (CVD): This method uses like silica-based wafer to heat at a high temperature a carbon-based gas in the presence of metal catalysts. As the high temperature breaks the gas carbon bonds, the metallic catalysts anchor each carbon atom to the surface growing outwards longer forming a nanotube. CVD is the most used method because of its large quantity production and low cost relative to the other techniques. (Szabó, 2010)

2.2.2 Application of CNT in the construction sector

As nanotechnology, being the 21st industrial revolution and a fast growing sector (Siegel, 1999) it will change the way we understand, make, control, and design things over the atomic nanoscale level. In today's world, different disciplines such as electronics, mechanical, environmental, biology, genetics, aeronautics, and many other fields already started to use nanotechnology. On the other hand, the construction industry is lagged compared to other industries. Even though the construction sector was classified as a promising area for nanotechnology in the early 1990s (Gann, 2002) and it is expected to be one of the highly influenced industry in the coming 10-15 years (Realis, 2002). There are many influential and extraordinary nano-materials having different properties, which are suitable to use in the construction industry. In this study, among the many only Carbon nanotube (CNT) will be explained further.

CNT have a remarkable property as discussed in the introduction section. Recently, the demand for the use of CNT is increasing while the market is rising exponentially. The application area of CNT is growing through time to list some of its use as a thermal material, energy storage, field emission, air and water filter, fiber and fabric composite, biomedical application and as a composite in the ceramic, polymer and construction sector. To list some of

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the filed applications, which have been done recently, flat display, screens, chemical sensors, hydrogen storage, actuators, nanocomputing chips and nanothermometers.

In the concrete technology mostly the use of CNT focus on its fiber reinforcement capability due to the high aspect ratio of CNT which range from 1000 to 10000 (Li, 2015). By the addition of small amount of CNT, less than one percent of the binder content in the mix, the compressive strength, flexural and dynamic modulus of the concrete will increase significantly as discussed earlier in this chapter. Even though, there is a difficulty on dispersing the CNT across the matrix fairly without affecting the property of the CNT and limiting its use at its full potential. In addition to the mechanical property enhancement, the electrical property of the cement composite will also be improved. The conductivity, stability, and piezoresistivity of the composite tremendously increase. On the other hand, the effect of CNT on the chemical property level to the hydration products are not still clear, and there are little studies on the effects but some papers claim that it will activate and increase the formation of hydration products. This paper also tries to clarify the effect of CNT on the hydration products. Furthermore, CNT cement reinforced composites have some practical application such as a composite sensor, non-distractive civil structure health monitoring system and as heating of buildings (Saez et al., 2006; Li, 2005).

2.3 Silica fume

Silica fume is a byproduct while burning the raw materials quartz, coal and woodchips in an electric furnace producing smoke in the production of silicon metal or ferrosilicon alloys. The collected smoke from the furnace is silica fume. The individual particle size of the silica fume is very small around $1/100^{th}$ (13,000-30000 m^2/kg) of an average single cement grain.

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With such a small particle size, the surface area of the silica fume increases, which makes it a very reactive pozzolanic material in the concrete. Even though it is known that silica fume increase the concrete strength and durability, but still there is doubt on the exact way how the silica fume affect the strength (De Larrard, 1993).

The reactivity of silica fume is highly dependent on the finesse of the particle as filler and the amorphous silicon dioxide content (Razak and Wong, 2005). This property of silica fume can be seen in three basic effects first it will refine and densify the matrix second it will react with the free lime (CaO) from the hydration product, and the last one is that its refinement capability on the ITZ (Khan and Siddique, 2011). The fact that silica fume will react with calcium hydroxide, lead to a high chemical shrinkage (Jensen and Hansen, 2001). Leading both cement and silica fume to a high bulk shrinkage (Lura, 2003). The main physical and chemical properties of silica fume are shown in Table 2.2.

Table 2.2 Chemical and physical property of silica fume (Khan and Siddique, 2011; panjehpour et al., 2011)

Physical property (Silica fume Association, 2014)					Major chemical composition (Personal estimation made after referencing various published data's)				
Particle size (μm)	Bulk density (as-produced) (Kg/m^3)	Bulk density (densified) (Kg/m^3)	Specific gravity	Specific surface area (m^2/kg)	SiO_2 wt%	Al_2O_3 wt%	Fe_2O_3 wt%	MgO wt%	CaO wt%
<1	130-430	480-720	2.2	15,000-30000	>85	<2	<2	<1	<1

2.4 Degree of hydration

Hydration reaction is the reaction chemistry of water and cement. The degree of hydration is the amount of already reacted cement percentage with water and Hydration kinetics is often

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represented by the rate of change in the overall degree of hydration. These three things are much related. The reaction of cement with water is followed by an exothermic reaction (heat realize to the outside) and water bound by a physical and chemical way to the hydration products. Based on these two things (heat realize and water bound) during the hydration reaction, the measurement of the degree of hydration is established. The two well-known conventional methods to measure the degree of hydration is that one based on the exothermic reaction that is by measuring the cumulative heat liberated during the reaction this method is referred as Isothermal calorimeter method. The second method is based on the bounded water measurement in the cement paste, the degree of hydration can be determined based on the amount of the bounded water. In general, by determining the degree of hydration, it will be easy to predict the durability and mechanical properties of a hardened specimen.

2.4.1 Mechanism and rate of cement hydration

2.4.1.1 Mechanism of cement hydration

The hydration mechanism of cement and water can be discussed in two phase. The first phase commonly termed as through-solution hydration or dissolution hydration. As the name implies in this stage, anhydrous cement grains dissolves, liberating into their constituent ion through the water forming a pure solution. Initially, the aluminate hydrates in a faster and great extent than the silicate while the cement grain is in contact with water, to slow down the rate of aluminate hydration gypsum is used as a reducer. This stage is mostly dominant in the early stage of hydration reaction. At the end of this stage, concentration increase and reached a supersaturated condition restricting the ionic mobility creating a favorable condition for the second phase, termed as, topchemical or solid-state hydration of cement. The second phase

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occurs mainly on the surface of the cement particle. In this phase, the concentrated ions in the solution started to precipitate forming a new solid product different from the initial minerals called hydration products (Mehta and Monteiro, 2006).

2.4.1.2 Rate of cement hydration

There are about four stages usually known during the rate of cement hydration over time from the initial time of water and anhydrous cement contact, which from the initial rapid reaction until the final steady state reaction (Lura, 2003). Figure 2.2 shows simple time versus the rate of heat evacuation diagram during a hydration reaction.

Stage .1 This stage is the fastest one approximately it will finish within 15 min after water and cement initial contact. The reaction is mainly governed by the calcium aluminate (alite), C_3A and gypsum with water to form ettringite. In addition, this stage is responsible for the loss of consistency and setting time of a hydrated cement paste even though it is determined by the amount of aluminates present in the reaction in the future stages. In the graph, it indicates the initial pick.

Stage .2 Usually referred us dormant period due to its low hydration product formation. It lasts for several hours during this time it forms a protective layer circling the cement grain, which limits further hydration showing that this stage is responsible for the formation of the plastic state, which allows the concrete to be transported and cast for several hours. Setting also starts at the end of this phase.

Stage .3 After the dormant period the principal hydration compounds begin to harden and the heat will increase again due the tricalcium silicate and dicalcium silicate reaction with

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water. This reaction is responsible for the strength formation since it produces calcium silicate hydrate (CSH) and calcium hydroxide (CH). This stage has relatively wider pick than the initial stage since it takes hours and sometimes days until the next phase.

Stage .4 Due to the formation of a dense layer of hydration products in stage 3 the diffusion of ions will be restricted leading to the decrease in the heat evolution until it reaches a steady state rate. Note that the hydration reaction will occur in the future as long as anhydrate cement components and water are in contact.

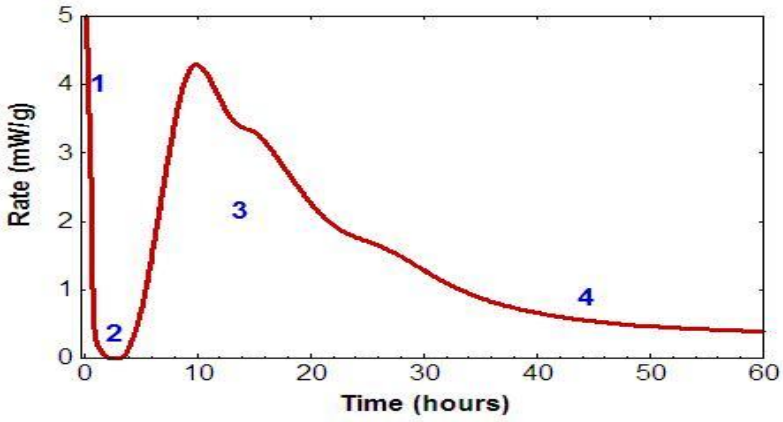

Figure 2.3 Schematic drawing of rate of hydration (www.iti.northwestern.edu)

2.5 Shrinkage

In general, shrinkage is water movement and moisture loss within and outside of the cement paste matrix by a different mechanism. There are different kinds of shrinkage some of them are dry shrinkage, autogenous shrinkage, chemical shrinkage, plastic shrinkage, thermal shrinkage and carbonation shrinkage. All types of shrinkage have their own way of shrinkage mechanism despite some relations between them. In this section, only the two types of

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shrinkage, drying shrinkage and autogenous shrinkage will be discussed including their mechanism of shrinkage.

2.5.1 Types of shrinkages

2.5.1.1 Dry shrinkage

The basic standpoint of dry shrinkage is to know that concrete is in a thermodynamic equilibrium with the surrounding environment. By that, when the environment around the concrete has a lower relative humidity than the inside relative humidity of the concrete water will diffuse from the concrete to the surrounding to maintain the thermodynamic equilibrium condition. During this process, water tends to leave from water containing capillary pores and mesopores (finer pores). By the diffusion of water from the finer pores, a macroscopic contraction occurred, which is referred as a dry shrinkage. Note that drying shrinkage is occurred after once the concrete reached a hardening point as it may confuse with plastic shrinkage which is evaporation of water before setting of concrete due to higher outside temperature and evaporation rate than the concrete surface. The theoretical prevention method for dry shrinkage is maintaining 100% relative humidity, which is impractical to apply. However, keep in mind that there are many reduction mechanisms available.

2.5.1.2 Autogenous shrinkage

This type of shrinkage is mainly dominant on a low water to cement ratio concretes. Autogenous shrinkage is a small external volume change before hardening. The low amount of hydration products in the mixture than the original hydration products (cement and water) initiates the use of waters filled in the capillary pores for further hydration. However, when the

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hydration products cannot fill the pores fully relative humidity inside pore space will decrease. This induces a depression on the pores, which lead to a compression in the solid phase (bissonnette 1996). Note that autogenous shrinkage in a normal or high water cement ratio concrete is low, insignificant, and mostly difficult to differentiate it from the drying shrinkage. The theoretical prevention method of autogenous shrinkage is to supply a continuous water to keep the capillary pores all time filled.

2.5.2 Mechanism of shrinkage

There are many different concepts proposed in the mechanism of shrinkage that is still open for discussion and not confirmed yet. In this section, only the two known theories related to our topic will be discussed that is the capillary stress and disjoining pressure shrinkage.

2.5.2.1 Capillary stress

The basic principle of the capillary stress shrinkage mechanism is based on the Laplace's and Kelvin's equation. Based on Laplace equation the change in the internal hydrostatic pressure (P) is indirectly proportional with that of the radius of the meniscus. The Kelvin equation stipulated that the vapour pressure (P/Po) and the radius are inversely proportional. Based on the two equations the stress increases as the radius of the meniscus decreases, in other words, the smaller the pore size the higher the stress induced. The limitation of this theory is that it cannot explain the shrinkage occurred in pores with less than 2.5nm since meniscus cannot be formed below this size (young et al, 2001).

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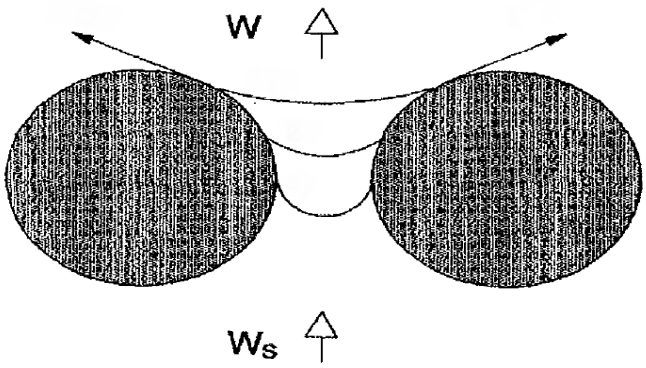

Figure 2.4 A schematic diagram on capillary stress (Radocea, 1992)

2.5.2.2 Disjoining pressure

In this theorem, water moves through the capillary pores from the voids to maintain the hygrometric balance during the free movement of the water a disjoining pressure decrease between the solid particles leading to a volume contraction in the paste (powers, 1968). The disjoining pressure usually described and measured by attractive and repulsive forces to explain a complex relation between water and two solid surfaces (Wittmann et al., 2009). In addition, this pressure can be expressed in terms of change in chemical potential too because disjoining pressure depends on the change of surface energy change and the ionic concentration in the water (Beltzung and Wittmann, 2004). In figure 2.5 below a schematic representation of the disjoining pressure is shown when two surfaces are in Vacuo (figure.2.5a) and an aqueous solution (figure.2.5b).

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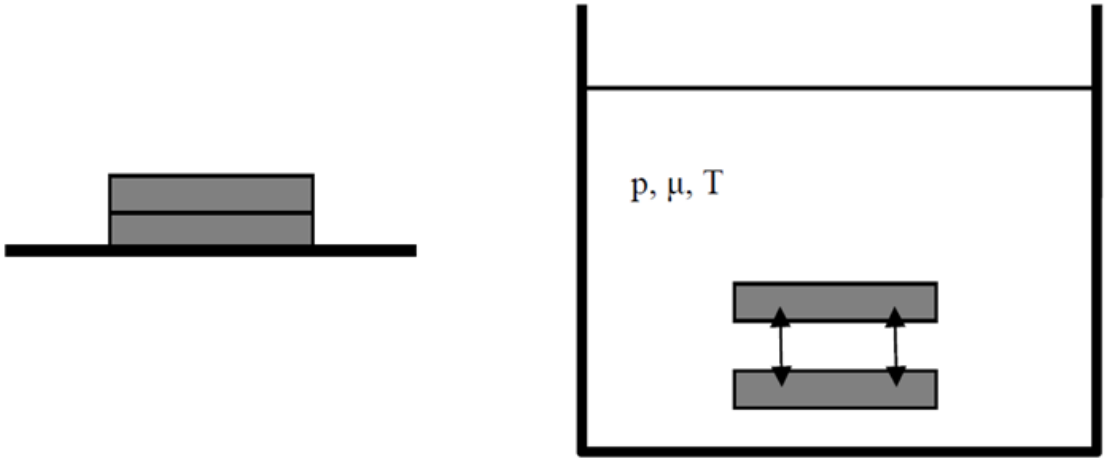

Figure 2.5 Schematic diagram on disjoining pressure (a) particles in vacuo (b) particles separated by disjoining pressure in a liquid (Wittmann et al., 2009).

2.6 Literature review

As discussed earlier in this chapter the nanotechnology in the construction industry is a recently growing industry following that combining of nanomaterials such as carbon nanotube (CNT), carbon nanofiber (CNF), cellulose nanocrystals (CNC) and graphene with cement is rising aiming different purposes. In this research, the mechanical strength, shrinkage and hydration kinetics properties of hardened cement paste matrix combined with CNT will be studied. Even though, there are considerable amount of previous studies on the mechanical property effect of CNT on the other hand, the study on shrinkage and hydration kinetics effect of CNT is relatively limited. In this chapter, only the major points will be discussed in correlation with the main thesis points including desperation techniques and historical paths.

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The eye braking for CNT reinforcement in the cement paste matrix was theoretically stated by Makar and Beaudoin in 2003, at a conference in Scotland, on nanotechnology in construction (Makar, and Beaudoin, 2003). Based on the publication they stated the outstanding properties of the CNT if it is mixed in the cement paste matrix by observing under the scanning electron microscope (SEM) and by comparing the capability in other construction industrial works previously done. Suggesting that there will be expected mechanical strength improvement even tough, no mechanical results were included in the research.

Li et al., (2005) studied the effect of MWCNT in the cement matrix by treating the surface of CNT using a sulfuric acid and nitric acid at a ratio of 3 to 1 by volume to increase the bonding between the nanotube and the hydration products. In addition, a sonication was conducted to disperse the CNT. From the experimental investigation, the microstructure of the cement paste showed a densification by the addition of a 0.5% by weight of cement that in turn increase the mechanical property of the matrix for the functionalized CNT. (Li et al., 2005).

Cwirzen et al., (2008) used two type of MWCNT one in a pure form and the other one being functionalized with COOH group. In addition, solutions of polyacrylic acid and gum arabic were used to increase dispersion of the CNT beside the sonication process. As a result, almost all kinds of the mixtures showed an improvement in the compressive and flexural strength of the hardened paste regardless of the retarding effect of gum arabic on the fresh paste matrix without affecting the mechanical strength in latter ages (Cwirzen et al., 2005). Many other researchers also used sonication and different surfactants to disperse CNT in the Cement matrix and improve the mechanical property (Musso et al., 2009; Nasibulin et al., 2009; Wansom et al., 2006; Tyson, 2011; Abu Al-Rub et al., 2012 and Hunashyal et al., 2011).

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Table 2.3 Different researchers result on paste CNT composites

Researcher	CNTs (wt %)	Compressive strength (%)	Flexural strength(%)	Dispersion method
Cwirzen et al., 2005	0.024-0.042	35	14	Sonication and polymers
Luo et al., 2009	0.2	29.5	34.5	Ultrasonication and superficial active agents
Konsta-Gdoutos et al., 2010	0.04-0.08	–	25	Sonication and surfactant
Tyson, 2011	0.2	–	20	Sonication and polycarboxylate
Collins et al., 2012	0.5	-8	–	Sonication and surfactant
Wang et al., 2013	0.08	–	71	Sonication and gum arabic
Kim et al., 2014	0.15	30	–	Silica fume
Zuo et al., 2015	0.5	15	–	Sonication, NaDDBS, and 800rpm stirring

The tendency of CNT to agglomerate easily due to their high van der Waals forces caused by the large surface area of CNT which requires a fair desperation technique (Sanchez and Ince, 2009; Manzur, 2014). However, many papers claim that most of the dispersion techniques have their own limitations. For instance, most researchers used sonication as a desperation technique. However, some papers claim that these techniques lead to a creation of air bubbles on the cement matrix weakening the composite structure due to the surfactants in the sonication process (Yazdanbakhsh, 2009). In addition, it leads to fragmentation of the nanotube by reducing the aspect ratio (Lu, 1996). In addition, most chemical desperation techniques have an adverse effect on the hydration products weakening the durability and reducing the conductivity and piezoresistive property mostly due to the functional groups attached on the CNT reducing the contact point by covering it with C-S-H (Li, 2005;

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Nasibulina, 2012). Size reduction of cement particle using a ball mill machine has been found to increase the desperation of CNT throughout the matrix. On the other hand, reducing cement size have its own negative effects such as an increase in, thermal cracking, chemical shrinkage and autogenous shrinkage (Bentz, 1999). To avoid and minimize the adverse effects of dispersing CNT while using different techniques in the mechanical and electrical behavior of the cement matrix this research use silica fume with a fine particle size. Silica fume is intermixed with the CNT and CNF to separate the agglomerated CNT/CNF mechanically. Recent studies also support this technique (Sanchez and Ince, 2009; Kim, 2014).

As mentioned before, there are few resources on the effect of CNT on the shrinkage and hydration kinetics of cement paste. That initially initiates the work on this topic to be carried out. Most of the studies done on shrinkage are mainly considering the early age shrinkage of the paste matrix, which highly depends on the hydration reaction rate at the early age. Li et al., (2015) used four type of mix proportion in a paper while comparing only the control with 0.3% CNT mix for the dry shrinkage experiment, the selecting was based on the highest compressive strength from the mixtures at 28 days result. Additionally, the measurement was taken for seven days. Even though the experimental diversity is limited, the result showed a 39.9% reduction in shrinkage than the control mixture (Li et al., 2015). Blandine, (2016) investigate the autogenous shrinkage effect of pure and functionalized MWCNT for cement paste with a CNT to cement proportion of 0.1% and less by weight of cement. The result was collected for 50 min after mixing. Based on the results, all the mixtures show lower early shrinkage than the reference mixture (Blandine, 2016). Konsta-Gdoutos et al., (2010) discuss the effect of short and long MWCNT effect on the autogenous shrinkage in the early days (4 days). Based on the result all the mixtures show a reduction in the shrinkage (Konsta-Gdoutoset al., 2010). Note

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that almost all studies were focused on the early age study on both the dry and autogenous shrinkage. In addition, except the Li, (2015) study that uses ball-milling dispersion, the rest uses the sonication technique as a major dispersion mechanism in addition to the functionalizing and use of surfactant.

Even though, there are a few literatures in the hydration properties of the CNT composite most of them focus on analyzing the hydration based on the morphological study using the SEM images and porosity distribution on the matrix indirectly. On the other hand, some papers studied directly by evaluating the rate and degree of hydration. petruninet al., (2015) investigated the interaction between CNTs and hydrate ions based on a theoretical and experimental study using a pure and carboxylic functionalized MWCNT by XRD and quantifying each hydration products were done using Rietveld method to compare the effect. Based on the result, the functionalized CNT increases the concentration of C-S-H gel and according to the theoretical explanation, the "CNT acts as the center of crystallization for the hydration products" (petrunin et al., 2015). Yizheng Cao., (2014) studied the effect of CNT and CNC on the cement paste matrix in detail mainly focusing on the CNC. The study undergoes different kinds of experimental analysis such as Isothermal Calorimetry (IC), thermogravimetric analysis (TGA), mercury intrusion piziometery (MIP), SEM, EDX and Rheological experiments. Based on the observation from the results it verified the bridging effect of CNT embedded on the hydration products (Cao, 2014).

2.7 Summary

In this chapter, a brief overview is done on the basic foundational concepts and materials of this thesis for a better understanding of the next chapters. In the introduction section, a

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highlight was made on Nanotechnology current and future roadmap followed by the nanomaterials used in this research, CNT and Silica fume, a brief introduction were made with respect to their property and way of production.

For a better grasp of the thesis the two main parts, the degree of hydration and shrinkage are explained well considering the future details in the thesis while avoiding unnecessary details. The main terminologies of both the degree of hydration and shrinkage were termed. In addition, the different mechanism and stages of hydration were briefly explained in this section including types of shrinkage and well known mechanisms of shrinkage proposed by different scholars.

Reviews of different works on the CNT were summarized for comparison. Even though there is a limited study in the area and finally the application area of CNT were discussed into two parts generally in the nanotechnology level and specifically in the construction sector.

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Chapter 3. Engineering property of cement paste incorporating MWCNT

3.1 Introduction

In this chapter, the engineering properties of the cement paste matrix incorporated with CNT will be discussed briefly. Detail analysis on the results of engineering property will be done through the next chapters including their relation and effect on the shrinkage and hydration kinetics of the matrix.

Tests included in this section are flowability, compressive strength, flexural strength and young's modulus. A discussion has been done for all the tests including by what standard method the test was conducted, and the results are discussed followed by a conclusion on the effect of CNT on the mechanical strength of the specimens.

3.2 Material and method

3.2.1 Material

The MWCNT samples used throughout the experiment were prepared by Hyosung Inc., using a production method of thermal chemical vapor deposition (CVD) process. The CNT products have a high percentage of purification 95% and more with a diameter range of 12-40 nm and a length around 10 μm. Silica fume was purchased from Elkem Materials Inc., (EMS-970 D) containing a high amount of SiO_2 above 90%. The surface area of the silica fume is 19,620 m^2/kg and Type I portland cement used in the experiment have a surface area of 352 m^2/kg both measured by Blaine test and Teller Method, respectively. In addition, a high range water reducer, polycarboxylic acid-based (COOH) superplasticizer was used to reduce the water without losing the fluidity of the cement paste matrix.

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3.2.2 Mix Proportion

Two types of water to cement ratio is used in the experiment, 0.25 and 0.4 each with a different CNT composition of 0%, 0.3% and 0.6% by weight of cement having a total of 6 different mixtures as shown in Table 3.1. Keeping cement weight constant the amount of silica fume and superplasticizer is fixed as 10% and 0.8% of cement even though, the superplasticizer was used only in case of 0.25 water to cement ratio mixtures. Some specific mix designs were adopted from a previous study by the author on enhancing the effect of silica fume in dispersing carbon nanotube showing the optimum amount of silica fume for a good desperation of CNT is 10% by weight of cement, which is also the same in this study too (Kim, 2014). The amount of CNT was fixed by investigating previous papers with suggestions of optimum ratios. When the amount of CNT increases above 1% by weight of cement, the porosity of the cement paste will drastically increase. In addition, the increase of the water-cement ratio has a decreasing effect on the desperation of both the CNT and silica fume by reducing the collision frequency between the two particles (Kim, 2014; Sanchez and Ince, 2009).

Table 3.1 Mix proportion in weight ratio

Mixture	Water	Cement	Silica fume	CNT	SP
w/c-0.25 C-0	0.25	1	0.1	0	0.01
w/c-0.25 C-0.3	0.25	1	0.1	0.003	0.02
w/c-0.25 C-0.6	0.25	1	0.1	0.006	0.03
w/c-0.4 C-0	0.4	1	0.1	0	-
w/c-0.4 C-0.3	0.4	1	0.1	0.003	-
w/c-0.4 C-0.6	0.4	1	0.1	0.006	-

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3.2.3 Method

3.2.3.1 Flowability

Flowability measurement was taken based on the ASTM C1437 standard by a flow table test. The flow mold used in the experiment have an upper diameter of 70 ± 0.5 mm and a diameter of 100 ± 0.5 mm at the bottom having a conical shape with a height of 50 ± 0.5 mm. Details about materials used during the experiment are illustrated in ASTM C230. During the sample preparation, the mixture was tamped 20 times to fill uniformly the flow mold after that the sample is placed in the center of the flow table and bounced (Dropped) 25 times within 15 Sec as per the ASTM C1437 standard and the diameter is measured in mm using a ruler. Figure 3.1 shows the materials used during the experiment. Note that measurement was taken immediately after casting and each mixture was carried out two times for a good precision.

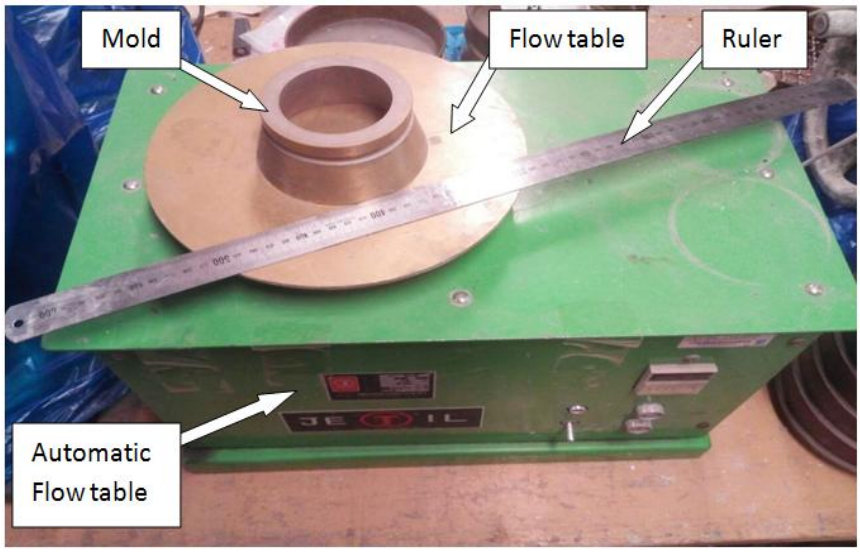

Figure 3.1 Apparatuses used during flowability measurement

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3.2.3.2 Compressive and flexural strength

Both the compressive and flexural strength were conducted with the same specimens at once following the ASTM C 348 standard test method for both. A prism shaped 40 by 40 by 160-mm specimen were casted for 3, 28 and 91 days measurement and details on the preparation specimens is discussed in ASTM 109. Each mixture has three samples for measurement all were demolded within 24 hours after casting and were plastic sealed until their measurement day. Initially, the flexural test was conducted as shown in figure 3.2. The flexural test is conducted based on the ASTM C348 by the center-point loading method as shown by the schematic diagram including all dimensions used while performing the test (figure 3.2-b). The flexural calculation was done using a specified formula from the standard as shown below. Note that an additional sensing instrument was used to stabilize the high fluctuations of the flexural test results and initial measurement were taken in kilogram (Kg) and then converted to Newton (N) by multiplying it by 9.8m^2/sec.

$$S_f = 0.0028P \quad \text{..... (ASTM C-348)}$$

Where: S_f is the flexural strength in MPa and P is the maximum load in Newton (N).

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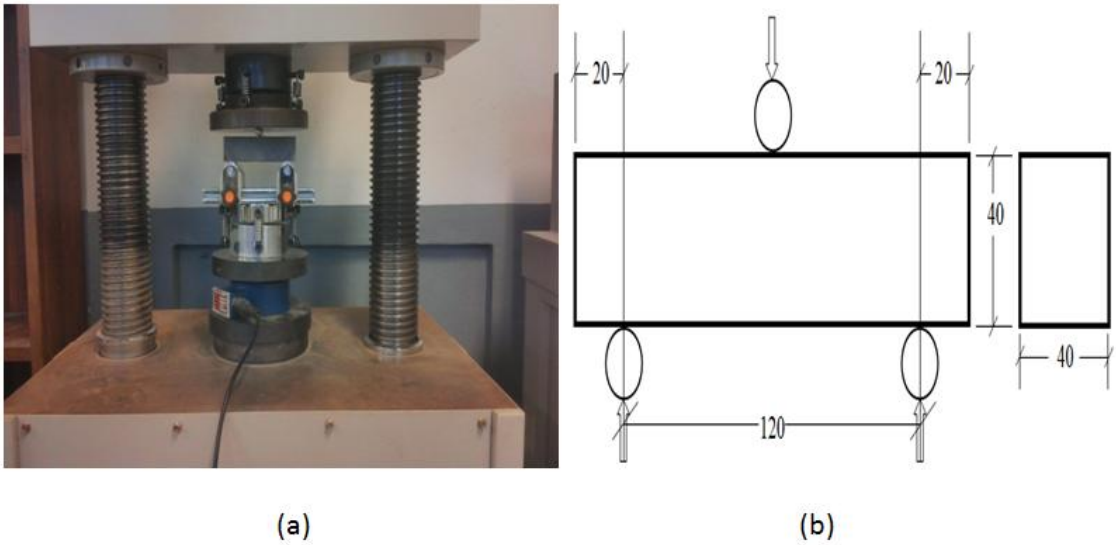

Figure 3.2 Flexural test setup (a) setup picture (b) schematic diagram

After the flexural measurement, the broken specimens were used to measure the compressive strength. The centroidal point were taken for the broken specimens and placed in the center point for the measurement as shown in figure 3.3. To calculate the compressive strength both the broken specimens were measured and add as one and divided by the total area of the original sample. Note that all results were taken in Newton this time. No addition instrument is used.

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Figure 3.3 Compressive strength test setup

3.2.3.3 Dynamic young's modulus

The dynamic modulus was measured by a nondestructive test method using the same specimens used to measure the flexural and compressive strength (40 x 40 x 160-mm) following the ASTM C 215. The measurement was done by impact resonance method with the longitudinal mode. During measurement, the specimens were hite on one side by an impactor and the response is received by a lightweight accelerometer from an opposite side of the impactor, while on both sides keeping the center point. An accelerometer less than 3 gram is attached to the specimen and used to amplify the signal to get a clear result by reducing the environmental influence. In addition, a towel was used under the specimen to reduce any vibration from the supporting frame (Table) as shown in figure 3.4. After the final output of the oscilloscope, the fundamental frequency (Natural frequency) is used to calculate the result using a standard set in ASTM C215.

$$E = DM(n)^2 \quad \text{..... (ASTM C- 215)}$$

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$$D = 4 \times (\frac{L}{bt})$$ ..... (ASTM C-215)

Where: E is the dynamic young's modulus in GPa, L is a length, b and t cross sectional area of impact applied in meter (m) , M is the mass in Kg and n' is the natural frequency in HZ.

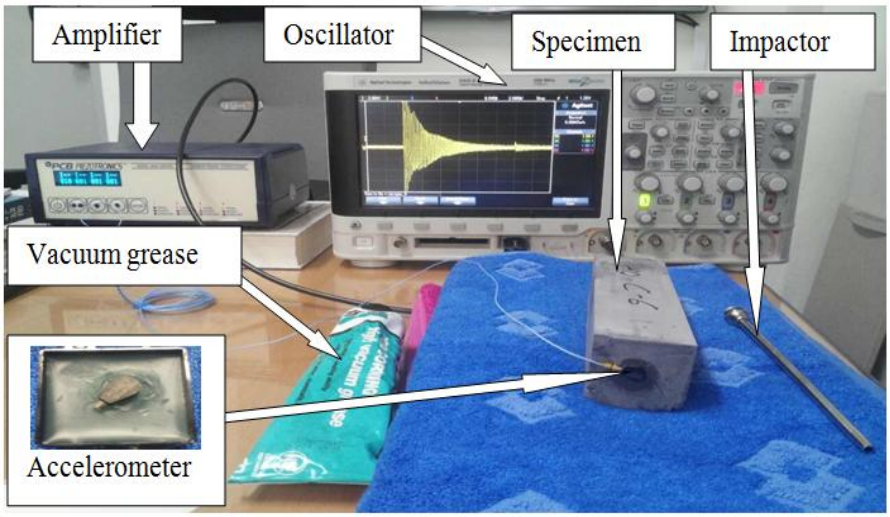

Figure 3.4 Dynamic modulus measurement setups

3.3 Result and discussion

3.3.1 Flowability

Flowability was conducted based on table flow method. Figure 3.5 shows the result of the flowability. In general, the result shows the addition of CNT to a mixture have decreasing effect on the flowability while compared to mixtures without CNT. The 0.25 water-cement ratio mixtures flowability show a linear decrease when the amount of CNT increases in the mixture. In percentile, the matrix with 0.3% CNT decreased by 12.5% and the 0.6% CNT by 17% compared to the plain mixture (0% CNT). Even though, the amount of the SP increased in the mix while the CNT increased in the mixture, whereas the result shows an inverse result

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from the expected one, an increase in flowability, which indicates SP might be physically absorbed by the CNT. The absorption will be discussed later in this section briefly. In addition, water may draw into the nanotubes due to the strong capillary force and the nanotubes can effectively hide it from the rest of the mixture (Manzur et al., 2014). On the other hand, flowability of 0.4 water to cement ratio mixtures also shows a decrease compared to the plain mixture by a 22% and 10.5% for the 0.3% and 0.6% CNT, respectively. Note that in this case there is no SP added to the mixture while the flowability of both CNT mixtures (0.3% & 0.6%) still decreased compared to the plane mixture. The results showed a decrease in the flowability by the addition of CNT in both water-cement ratios. It is known that the addition of fibers in a concrete generally reduces the flowability despite the type of the fiber used (Mehta and Monteiro, 2006). In overall, the flowability for all mixtures was affected by the silica fume tendency to increase the cohesiveness effect, which makes a proper work difficult in addition to the high surface area of the silica fume (Berra, 2012; Lawler, 2007). However, the ability of the CNT to cover the surface of the silica fume may decrease silica fume and water contact, which tend to increase the flowability by increasing the amount of CNT.

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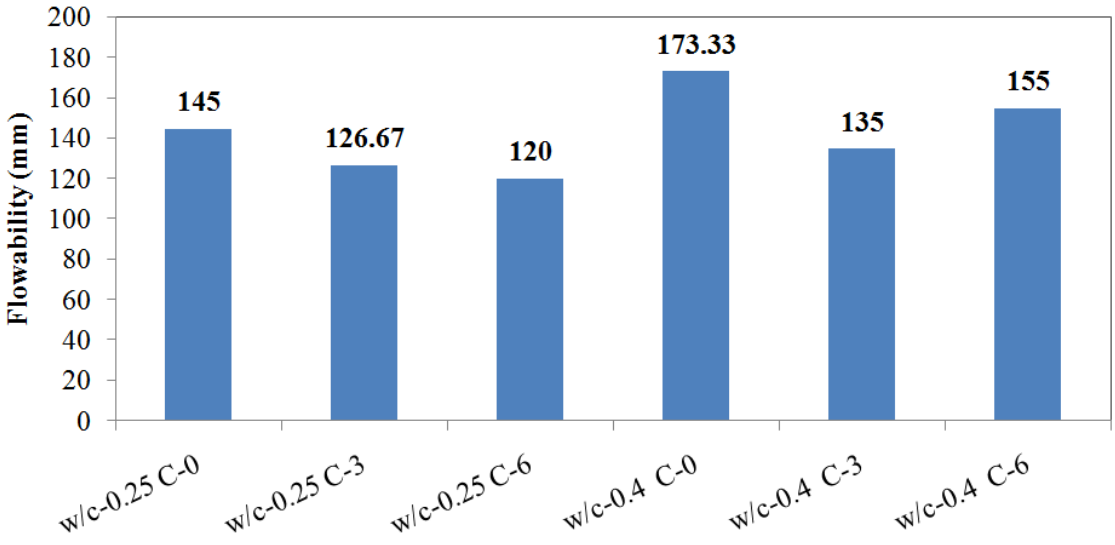

Figure 3.5 Flowability result of each mixture

To check if there is any additional chemical reason behind the decrease of the flowability FTIR spectra were taken for different samples. The samples measured are, raw CNT, CNT with water, CNT with water and SP, CNT with SP and the final one is SP. Figure 3.6 shows the FT-IR results. The spectrum as shown in the figure was taken at a range of 400-4000 cm^{-1}. The result of the Raw CNT in figure 3.6(e) showed no characteristic picks except the weak overtone bonds, however, while combining it with water and SP characteristic peaks were found at 1640 and 3330 the C=O and the O-H group, respectively. In addition, the SP shows peaks at 2920, 1460, 1340, 1240, 1080 and 940, the first three peaks confirm the SP^3 C-H stretch over and the pick at 940 shows an alkene base SP^2 C-H stretch the remaining picks indicating C-O stretch.

The different combination of the three samples CNT, water and SP purpose is to check if there is any kind of absorption of SP or water by the CNT. From the result, the characteristic

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picks of the pure SP have shown no intensity or broadness change of the curves while combining with CNT and while the three samples combined, the intensity of the characteristic picks on SP decreased which is due to dilution of the SP in the water. In addition, no broadness is seen on the curves. To conclude, neither the water nor the SP has a clear absorption by the CNT.

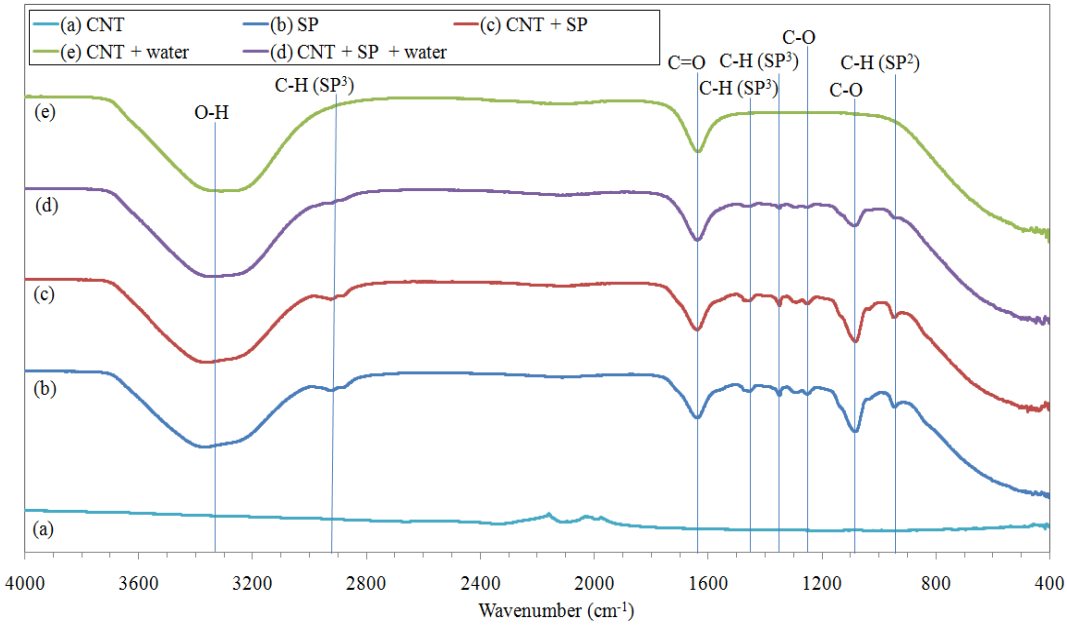

Figure 3.6 FT-IR pick results for each combination

3.3.2 Mechanical properties

3.3.2.1 Compressive strength

Figure 3.7 a and b shows the experimental values for 0.25 and 0.4 water to cement ratio respectively. Results were collected for 3, 28 and 91 days by sealing specimens with plastic until the measurement day. From 0.25 water-cement ratio result, it is clear that there is a

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reduction in strength while the amount of CNT increases in the mixture. For the 0.4 water-cement ratio mixtures containing CNT, on the other hand, showed the reverse, an increase in strength while amount of CNT increases and the plain mixture (without CNT) showed inconsistent result over time showing the lowest at 3 days and the maximum at 28 days as given in figure 3.7b. The test results of each mixture based on their standard variation show steady results for CNT containing mixtures relative to plain mixtures.

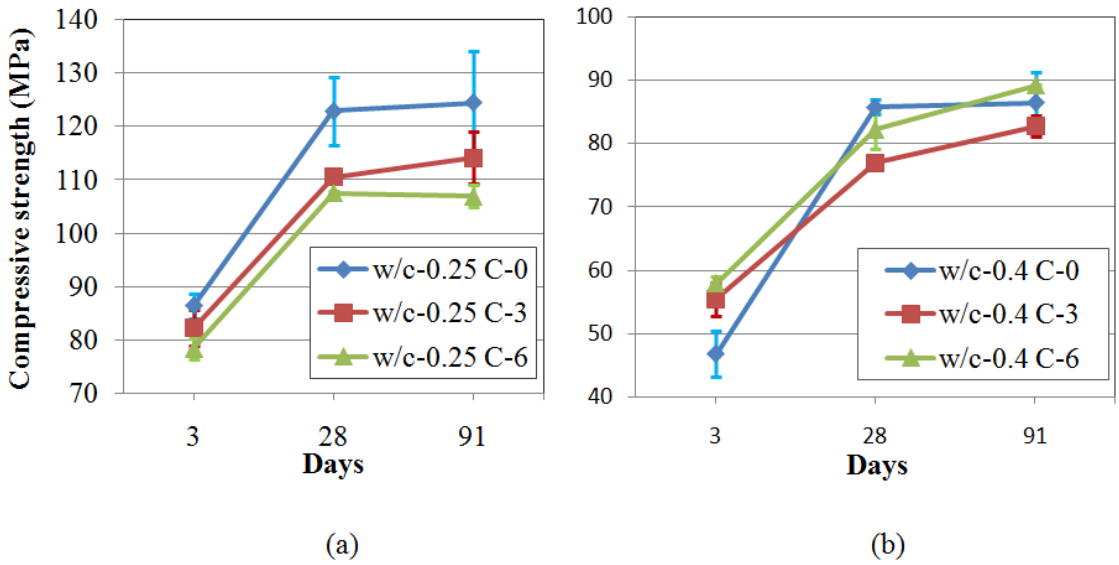

Figure 3.7 Compressive strength for 3, 28 and 91 days (a) 0.25 water to cement ratio (b) 0.4 water to cement ratio

A detailed study by Manzur .T et al., 2014 on the compressive strength of seven untreated commercialized MWCNT powders with different mix proportion have confirmed that the smaller size CNT will have a significant effect in increasing the compressive strength. This is due to its capability to distribute at a much finer scale and fill the nano-pores within the cement matrix. In addition, the agglomeration of CNT also has an effect on the strength.

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3.3.2.2 Flexural strength

Many studies claim that the flexural strength will increase during the incorporation of CNT in cement matrix (Wang et al., 2013; Luo et al., 2009). In this research, a significant increase in the flexural strength was shown in general except in the early days (3 days), which showed only a slight reduction and improvement for 0.25 and 0.4 water-cement ratio mixtures, respectively while the CNT containing samples are compared to the plain samples. However, the 28 and 91 days flexural strength has shown a significant increase in both water-cement ratio mixtures. The 28 days specimens show an increase of 77% for the 0.3% CNT and 0.25 water-cement ratio. In addition, another specimen with the same water-cement ratio and 0.6% CNT shows a 64% increase in the flexural strength. For the 91 days, the specimen with 0.3% CNT showed further raise up to 87% increase from the plain specimen. On the other hand, the 0.6% CNT shown a reduction from the 28 days measurement by 16.5% this also seen on 0.4 water-cement ratio specimens on both the 0.3% and 0.6% CNT samples. Likewise, the plain samples show a reduction in the flexural strength from 3 days to 91 days even though it is a slight decrease. It is complicated to explain the reduction of the flexural strength from the 28 days to 91 days for most of the samples. A study by Igarashi .S and Kawamura .M, on high strength mortars at a long age, showed the use of silica fume in a mixture has lowering effect on the flexural strength through time. This may be due to the late hydration of unhydrated cement grains, which gives rise to an internal expansive pressure in the microstructure (Igarashi, 1998; Larrard and Bostvironnois, 1991). In addition, the silica fume forms silica fields in the hardened paste as shown in figure 3.10 under SEM image. This silica fume field may produce a good condition for a shear failure during the experiment acting as a weak point.

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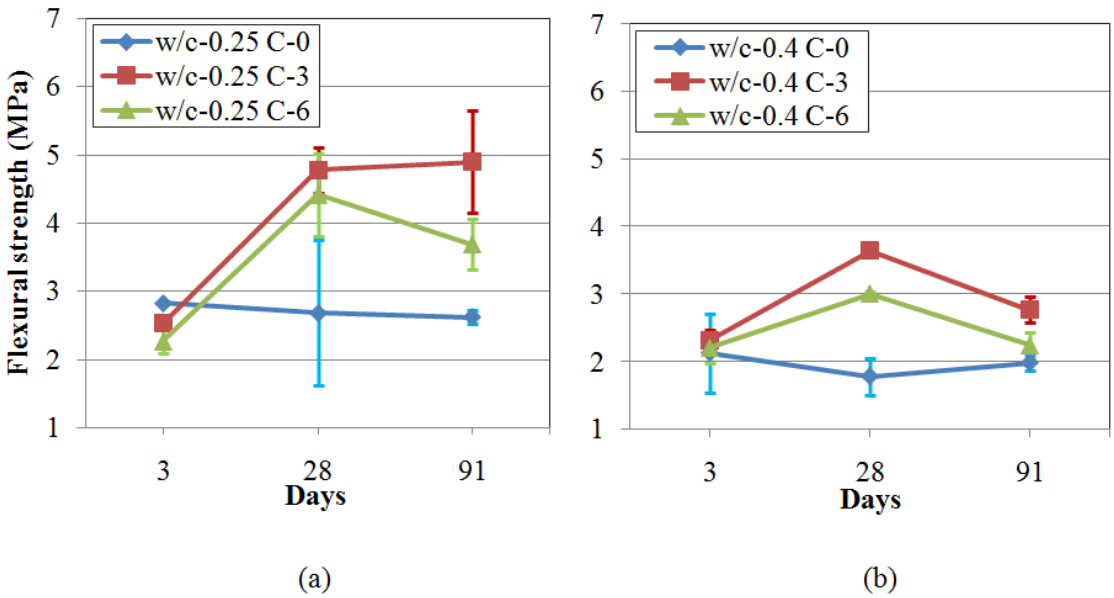

(a) (b)

Figure 3.8 Flexural strength for 3, 28 and 91 days (a) 0.25 water to cement ratio (b) 0.4 water to cement ratio

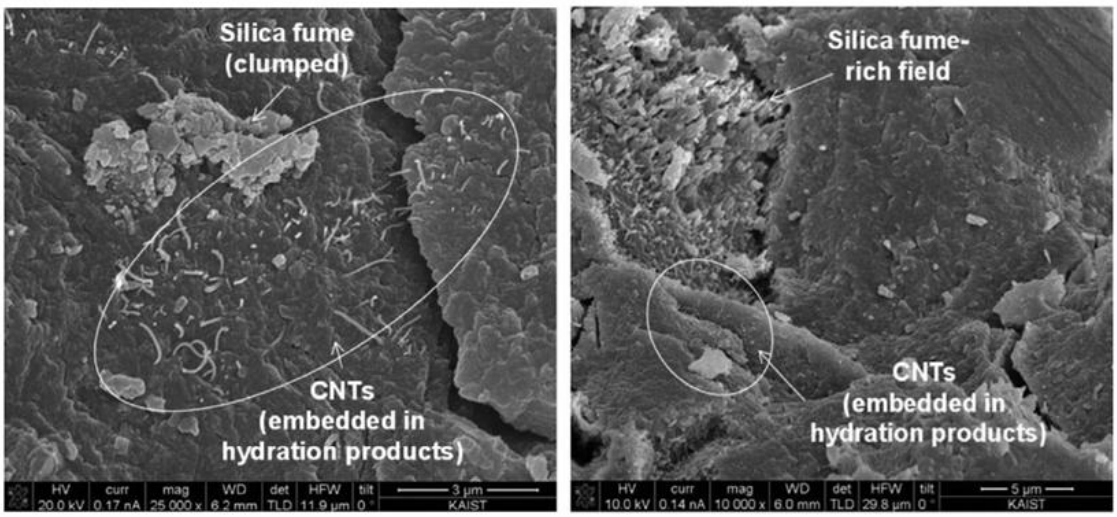

Figure 3.9 SEM image of silica fume fields in a CNT cement paste composite (Kim, 2014)

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3.3.2.3 Dynamic young's modulus

The dynamic modulus is a measure of stiffness in material and mainly used to characterize materials by quantity (Siddique, 2014; Constantinides, 2007). As discussed in chapter two previous studies show that the addition of CNT in a matrix could lead to an increase in young's modulus. This is due to the increase in stiffness on the C-S-H by effectively filling the areas with CNT (Chuah, 2014; Saez, 2006) which will be discussed in the next chapter in relation to the porosity in the hardened specimens. In this study, by the incorporation of the CNT unlike the compressive strength a significant increase were recorded and unlike the flexural strength, a continuous increase were recorded along the days. On the other hand, the plain specimens have shown degradation in some cases. This indicates that the CNT have a good filing property.

In the early ages (3 days) young's modulus measurement the 0.25 and 0.4 water-cement ratio mixtures show a different result an increase and decrease respectively were shown compared to their plain samples. In case of the 28 days modulus, the specimens with CNT show a significant increase approximately 14% and 17% for both 0.25 and 0.4 water to cement ratios, respectively for mixtures containing 0.3% CNT. Nevertheless, a further increase of CNT to 0.6% has shown a decrease compared to the 0.3% CNT samples even though it is higher than the plain samples. The same thing also observed on the 91 days specimens for 0.25 water-cement ratio. However, in the 0.4 water-cement ratio containing 0.3% CNT slightly overpass the 0.6% CNT containing mixture. Konsta-Gdoutos et al. also found that the further addition of longer size MWCNT would decrease the young's modulus. This may be due to the clamping of the CNT inside the paste by increasing the porosity inside the hardened specimens.

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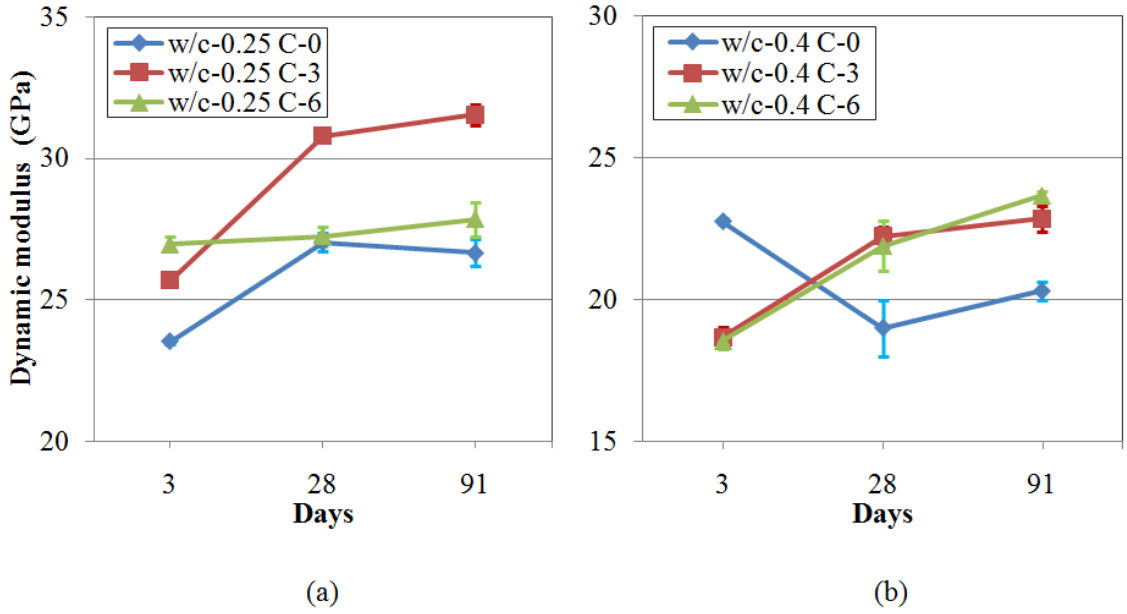

Figure 3.10 Dynamic young's modulus for 3, 28 and 91 days (a) 0.25 water to cement ratio (b) 0.4 water to cement ratio

3.4 Summary

In this chapter, the flowability and the mechanical strength were discussed briefly based on experimental observations by incorporating CNT in the cement paste matrix using 10% silica fume as a dispersion mechanism through the paste matrix. In general, from the result, these 4 points can be stated as a summary.

1. The flowability result shows the addition of CNT to the mixture have a decreasing effect on the flowability compared to the mixture with no CNT. This is mainly, due to the usage of any fiber in concrete will tend to decrease the flowability. In addition, the cohesiveness tendency of the silica fume has affected the flowability in general.

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2. The compressive strength for all the different mix proportions in the experiment shows a reduction unlike the flexural strength while the CNT is incorporated. In addition, while the CNT amount increase in the mixture the strength also decreased in most cases this might be due to the size of the CNT having a larger length. Despite the size, the agglomeration of CNT may also have influenced the strength.

3. Specimens prepared for the flexural measurement have shown an increase despite the fact that the 3 days result show a reduction that may be affected by the late hydration of the CNT incorporated specimens. However, the 28 and 91 days flexural strength have shown a significant increase up to a maximum of 77%. Even though it shows a decrease through time from 28 days to 91 days, this may arise due to the late hydration of unhydrated cement grains that give rise to internal expansive pressure in the microstructure. In addition to that, the silica fume fields that may act as a weak point for a shear failure.

4. By incorporation of CNT in the cement matrix, the dynamic modulus has shown an increase and a continuous increase along with the long-term age. This indicates that the matrix has a low porosity due to the effective fill of the CNT and the further stiffness of the C-S-H along with the increasing age. However, the further addition of more CNT has a decreasing effect, which might arise due to the formation of small CNT clamps in the mixture.

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Chapter 4. The effect of MWCNT on hydration kinetics and shrinkage

4.1 Introduction

As discussed in the second chapter studies on hydration kinetics and shrinkage properties cement matrix incorporated with CNT is few. By acknowledging the gap, this thesis tries to fill the gap. In the study, a detail investigation is done to analyze the hydration kinetics by measuring the degree of hydration and isothermal calorimeter. In addition, the hardened microstructure and chemical composition is investigated using MIP and XRD, respectively. In case of shrinkage, measurement was taken for autogenous shrinkage and dry shrinkage including the mass loss.

The above tests will be discussed in detail including, on what standard and method the tests are conducted. Finally, the results will be discussed and a conclusion is made. In addition, other supporting experiments will also be discussed throughout the chapter.

4.2 Material and method

4.2.1 Material and mix proportion

All the materials and the mix proportions used in this chapter are identical with that of the previous chapter (engineering properties).

4.2.2 Experimental method

An identical mixing procedure and method were applied for all the different kinds of specimen prepared in this study. Mixing was done by a standard Hobart mixer, as specified in ASTM C305. After pouring all the dry samples cement, silica fume and CNT, sequentially into

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the mixer dry mix were done for 3 min following that, water was slightly added within 4 min after the dry mix. After pouring all the water and SP an additional 3 min were mixed with a total of 10 min mixing time for each mixture. The superplasticizer for 0.25 water cement ratios was added immediately after the water was poured completely.

4.2.2.1 Porosity and XRD measurement of the hardened paste

The XRD samples of the hardened paste were prepared by crushing the samples to a fine powder with a ball mill machine at a speed of 600rev/sec and measurement were taken by X'Pert^3 Pro MRD (PANalytical, Netherlands). The porosity of the specimen measurement was done by mercury intrusion porosimetry (MIP). A specimen size of 1cm×1cm×1cm cubical specimen was prepared for the test.

4.2.2.2 Shrinkage Test

Sealed and unsealed condition was used to investigate the linear deformation using a rectangular specimen with a dimension of 25 mm × 25 mm × 250 mm (W×H×L). For each condition (sealed and unsealed) and mixture, type two specimens were used to test the deformation for 50 days starting from 24 hours after the placement of the fresh cement paste matrix in the mold. During the casting, the temperature was about 20 ± 1° C. After casting, all specimens were covered by a plastic cover in order to avoid any kind evaporation before demolding. Demolding was done after one day and the specimens for dry shrinkage were unsealed after one day from the plastic cover by exposing the specimen to the air. On the other hand, the specimens for autogenous shrinkage were kept sealed. Both kinds of specimens were kept at a constant temperature of 20 ± 1℃ for the entire measurement and the measurement

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was taken by a demec gauge with a pin attached to the surface of the specimens as shown in Figure 4.1. Note that the mass loss of each specimen was also analyzed side by side with the shrinkage measurement for the dry shrinkage specimens.

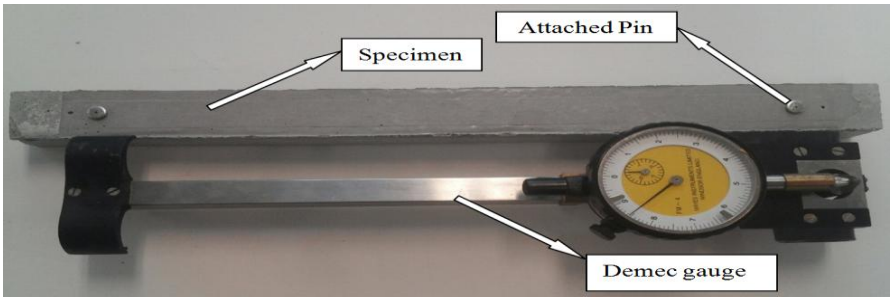

Figure 4.1 Shrinkage measurement apparatus

4.2.2.3 Degree of hydration and heat of hydration

To obtain the degree of hydration after casting the fresh mixtures were kept in a plastic vinyl around 200 ± 30 gram with a thickness of less than 5 mm for day 1, 3, 7, 28 & 91. The samples were covered in order to prevent water evaporation from the samples to the air. During the measurement day, samples were taken around 110 ± 20 gram from the plastic vinyl and dried at 110 ℃ on the oven for about 48 hours to check the mass loss evaporated from the sample based on the mass of specimens. The degree of hydration was measured indirectly as a non-evaporated water to cement ratio (W_{ne}/C) and the measurement method was adopted from H.K. Kim, 2013 (Kim, 2013). On the other hand heat of hydration were measured based on the ASTM C 1679 with an isothermal calorimeter. The temperature of each mixture was recorded starting from the moment mixing finished until the 7^{th} day by keeping the samples in a temperature-isolated container to regulate the external temperature effect to the minimum.

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4.3 Result and discussion

4.3.1 Microstructure of CNT reinforced cement paste matrix

The MIP is the most common way used to analyze the pore size distribution of hardened specimens at 3, 28 and 91 days in order to understand the pore size and distribution along with the relation to mechanical and shrinkage properties. Specimens without (0%) and with (0.3% & 0.6%) CNT had been analyzed in 0.25 and 0.4 water-cement ratio. From the result in Table 4.2, the total intruded volume of the paste matrix show a significant reduction from 3 days to 28 days and only a slight decrease or in some cases increase is shown from 28 days to 91 days. Except for 0.25 water-cement ratio with 0.3% CNT, that shows an odd result, high intrusion volume for 28 and 91 days than the 3 days result. Keeping the odd result out still, there is no much evidence to conclude that there is any decrease in the intrude volume due to the CNT compared to the plain samples.

Table 4.1 Total intruded volume result

Total intruded volume(ml/g)	w/c-0.25 C-0	w/c-0.25 C-3	w/c-0.25 C-6	w/c-0.4 C-0	w/c-0.4 C-3	w/c-0.4 C-6
3 Days	0.1099	0.0931	0.1392	0.2246	0.2194	0.2192
28 Days	0.0875	0.133	0.0951	0.1899	0.1855	0.1869
91 Days	0.0883	0.1316	0.0945	0.1843	0.1856	0.1906

By comparing, the relations of the total intrude volume to the compressive strength values, no direct relations were found. A previous study by Kim et al., 2014, showed that the relation

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is low (R^2<0.6) by contrasting with those studies that claim a higher relationship (R^2>0.85) (Kim, 2014). In addition, the study stated the relation might be affected by other factors such as dispersion of CNT and the interfacial interaction between CNTs and hydration products.

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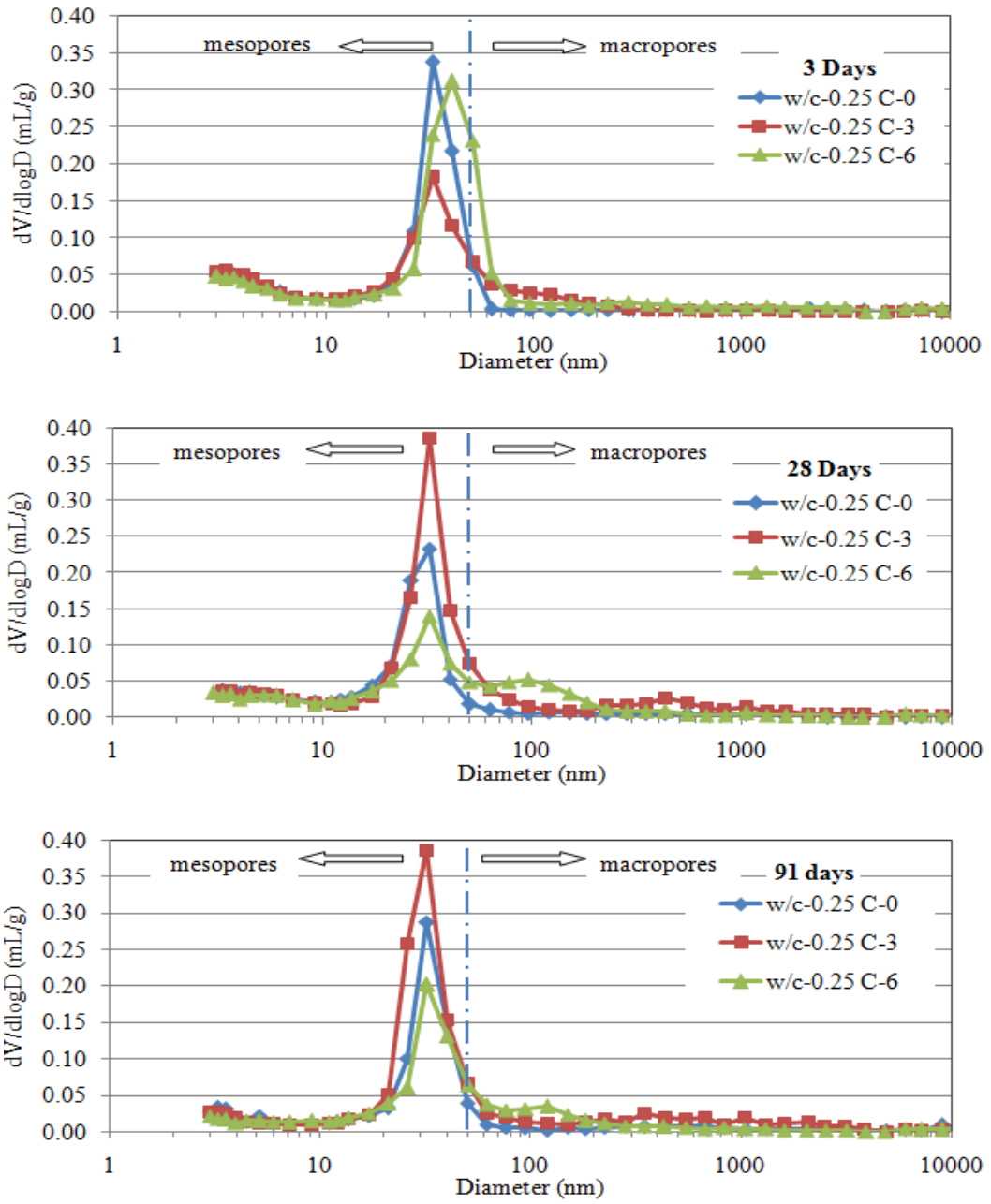

Figure 4.2 Pore distribution for 0.25 at 3, 28 and 91 days (top to bottom)

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Figure 4.2 and 4.3 shows the pore distribution graph for 0.25 and 0.4 water-cement ratios, respectively. From the result of 0.25 water-cement ratio a range of micropores mainly determining the capillary voids, around 10-50 nm, were observed. These pores show a shift towards the smallest range (mesopore) depending on the period of measurement and on the other hand, the shift is high relatively for 0.6% CNT mixture. The same shift was also seen for 0.4 water-cement ratio specimens towards to the smaller range, while the range is from 10 to 100nm. However, the plain sample shows a relatively steady situation compared to the CNT containing samples. In general, the addition of CNT despite its quantity shows a slight reduction in the macropores (>50nm) and a slight increase in the mesopores (2-50nm). Nevertheless, keep in mind that the total porosity increased for the CNT containing specimens. In overall, it is clear that the pore size and distribution is highly influenced by the silica fume rather than the CNT due to the Silica fume large surface area and high pozzolanic reaction. However, the further shift by CNT containing mixtures towards the mesopores shows the filler capability of the CNT.

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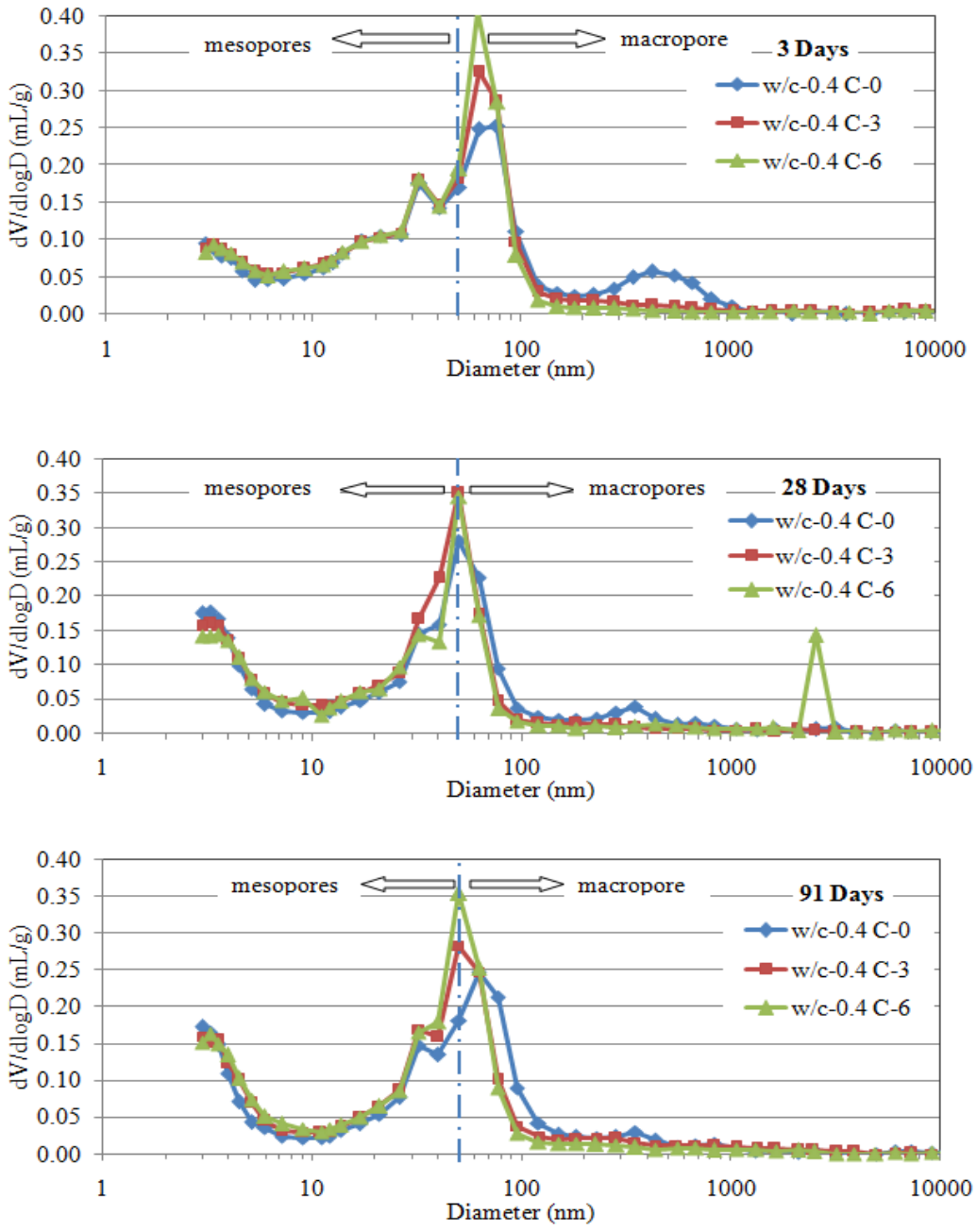

Figure 4.3 Pore distribution for 0.4 at 3, 28 and 91 days (top to bottom)

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4.3.2 Hydration kinetics

4.3.2.1 XRD analysis

To reason out the effects of the CNT on the porosity, shrinkage and mechanical strength effect it is critical to understand the effects of the hydration products through time. To analyze the hydration products XRD patterns are used at 3, 28 and 91 days as one of the techniques in this study. Figure 4.4 and 4.5 shows the hydration patterns for 0.25 and 0.4 water-cement ratio mixtures, respectively at different CNT contents (0%, 0.3% & 0.6%). Different picks have been identified as shown in the figures. However, the picks for the CNT and ettringite cannot be found in the XRD pattern this could be due to the amount of the CNT used in the mix is low to be detected clearly and the Ettringite formation might be influenced by the fast pozzolanic reaction of the silica fume due to its extreme fineness. In addition, the intensity of the quartz detected by the XRD pattern is low because of the silicon dioxide content in the Silica fume have a high amorphous phase (Khan and Siddique, 2011) which also explain the C-S-H pattern loss in the XRD due to its amorphous characteristic.

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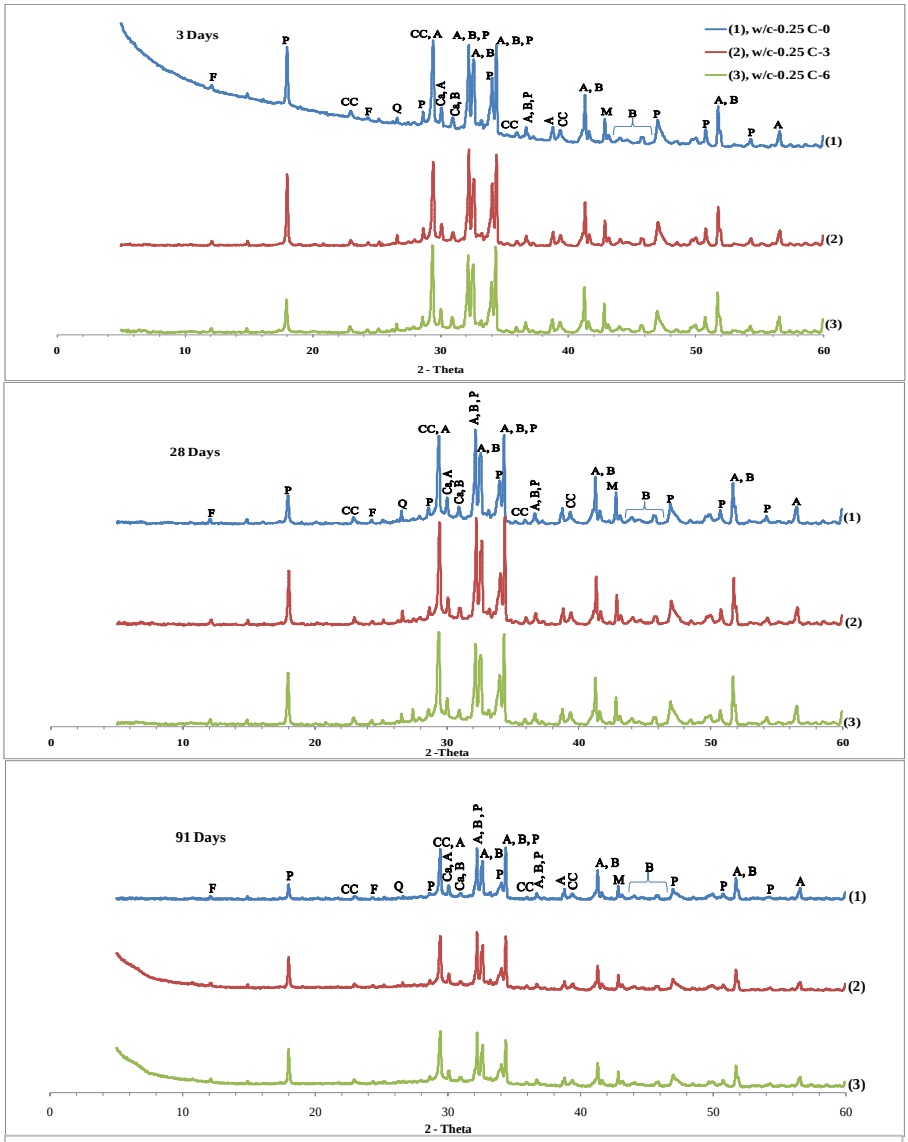

A- Alite, **B**- Belite, **Ca**-calcium , **CC**- calcite, **F**- Ferrite,**M**- Periclase, **P**- Portlandite, **Q**- Quartz

Figure 4.4 XRD analysis for 0.25 water to cement ratio at 3, 28 and 91 days (top to bottom)

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The XRD result on figure 4.4 show the 0.25 water-cement ratio samples at different ages. From the result, a high amount of Unhydrated cement (A, B) was shown throughout the ages in the plain samples compared to the CNT containing mixtures. Inverse to that, the hydration products (P, CC) were seen throughout the ages less in the plain samples compared to the CNT containing mixtures this can be clearly seen in the 91 days samples, in figure 4.4-c. Even though there is a slight difference in the 3 and 28 days including both CNT containing mixtures, however, it is not easily identified in the figure.

A different result was observed for the 0.4 water to cement ratio mixtures. Even though, it is difficult to compare the unhydrate (A, B) products because of the intensity decrease due to the high water content in this mixtures. On the other hand, it is easy to compare the hydration products (P, CC) since they are showing high intensity. From figure 4.5, it is clear that the hydration products are higher in the early day (3 days) for the CNT containing mixtures compared to the plain mixture. However, along with the age increase the plain mixtures hydration product intensity gets more similar to that of CNT containing mixtures. To generalize the above discussion, the CNT have the capability to activate the early age hydration in both water to cement ratio mixtures, however, this was not continuous for the 0.4 water to cement ratio at latter ages. The addition of CNT to a mixture has complex relations that make it difficult to say, only based on the XRD patterns. In addition, in this XRD analysis, there is no new peak observed for the CNT containing mixtures rather than the one observed in the plain mixtures, which shows that the CNT act as only a nano-filler material.

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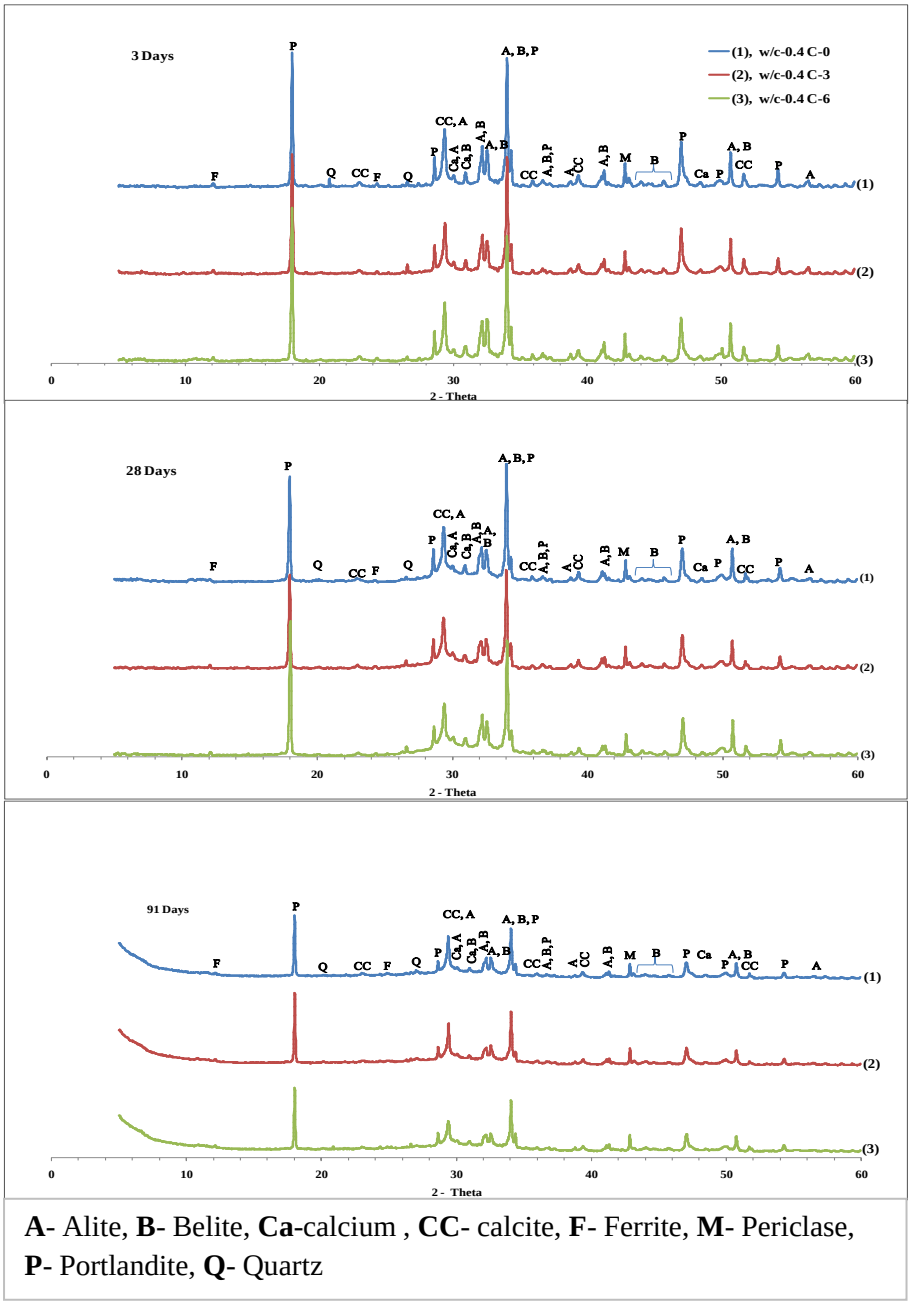

A- Alite, **B**- Belite, **Ca**-calcium , **CC**- calcite, **F**- Ferrite, **M**- Periclase, **P**- Portlandite, **Q**- Quartz

Figure 4.5 XRD analysis for 0.4 water to cement ratio at 3, 28 and 91 days

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4.3.2.2 Isothermal calorimeter

The isothermal calorimeter is used to evaluate the early age hydration effect and to understand the effect of the CNT amount in the mixture, which was difficult to tell by the XRD patterns due to a closer value in intensity to each other. Figure 4.6 shows the heat evolution in a temperature (℃) versus time (hour) graph. From the results, maximum temperatures are recorded for the 0.25 water-cement ratio mixtures with time delays between the mixtures. This happened due to the amount of SP added in the mixture showing the retarding effect of SP on the mixtures despite the intensity difference. On the other hand, since there is no SP in the 0.4 water-cement mixture there is no delay. In overall, both water-cement ratio mixtures have more or less similar temperature intensity especially the 0.4 water-cement ratio mixtures. The 0.25 water-cement ratio mixtures have an insignificant difference with a maximum difference of ±4 C^{o} and a decrease in the temperature intensity while the CNT percentage increases. In other words, a slightly lower hydration is shown while the amount of CNT increased in the mixture.

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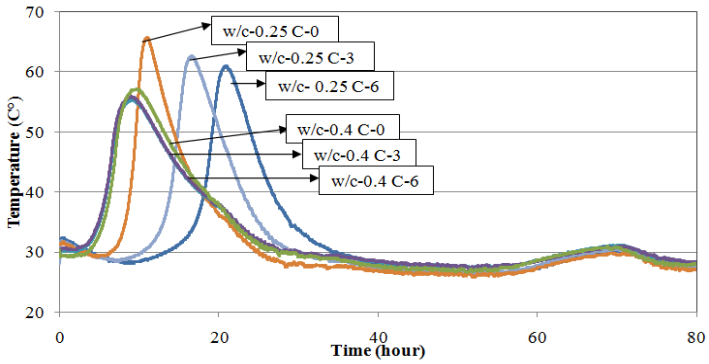

Figure 4.6 Isothermal calorimeter results for heat evolution versus time graph

4.3.2.3 Degree of hydration measurement

As discussed earlier in the material and method section this measurement method was adopted from H.K. Kim, 2013 et al. The degree of hydration was measured indirectly as a non-evaporated water-cement ratio (Wne/B). From the Graph in figure 4.7, a different result is observed compared to the previous XRD experiment discussed in this section. Except for 0.4 water-cement ratio with a 0.3% CNT content that shows a high content of non-evaporated water to binder ratio, the remaining CNT containing mixtures for both water-cement ratios show a decrease in hydration compared to the plain mixtures. The author thinks that the high thermal property of the CNT could facilitate easy moisture exchange with the environment affecting the total water content in the mixture before the measurement day. In general, the result confirms for the most part that the addition of CNT will decrease the hydration.

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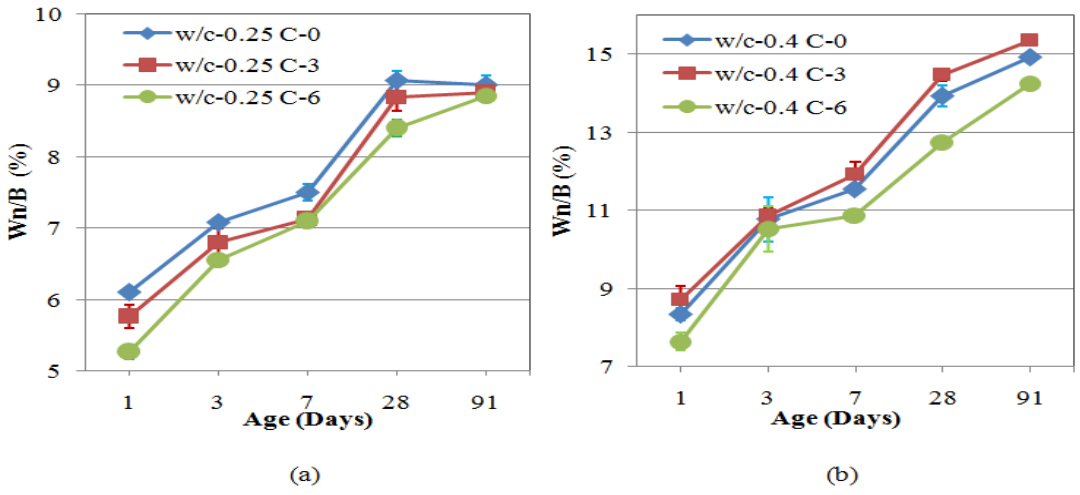

Figure 4.7 Degree of hydration measurement result at 1, 3, 7, 28 and 91 days

4.3.3 Shrinkage

4.3.3.1 Autogenous shrinkage

Figure 4.8 shows the shrinkage value for both 0.2 and 0.4 water-cement ratio mixtures. The result shows a compatible result compared to the mesopores (10-50nm) intensity observed in the MIP test in general. However, no direct relation is found. Autogenous shrinkage value has increased for CNT containing mixtures compared to the plain samples. This might happened due to the further hydration of CNT containing mixtures as shown in the XRD and results indicates that there is no enough water to fill the capillary pores. However, the amount of non-evaporated water measurement in the degree of hydration does not support the results on the shrinkage values.

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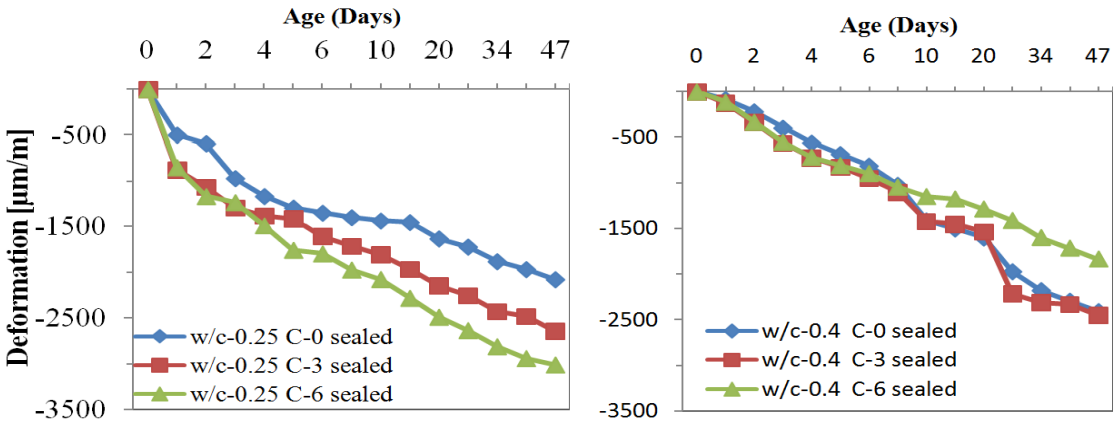

Figure 4.8 Result for the autogenous shrinkage

4.3.3.2 Dry shrinkage

The same result was shown in figure 4.9 for the dry shrinkage like that of the autogenous shrinkage despite the larger value deformation. The dry shrinkage value has increased compared to the plain samples for most of the CNT containing samples except for the 0.4 water-cement ratio mixture with 6 % CNT. These results were also clearly supported by the mass loss measurements in figure 4.9-b, which verify the shrinkage results and by the shift in the porosity result towards the mesopores while reducing the macropores. In addition, the result also indicates that a polymerization process might be activated by the addition of CNT. The increase in the shrinkage value and mass loss for most of the specimens containing CNT might be related to the experimental environment since dry shrinkage is highly dependent on the surrounding environment condition. In addition, the author thinks that the high thermal property of the CNT even in a bulk condition could facilitate easy heat exchange with the environment affecting the equilibrium condition with the specimens.

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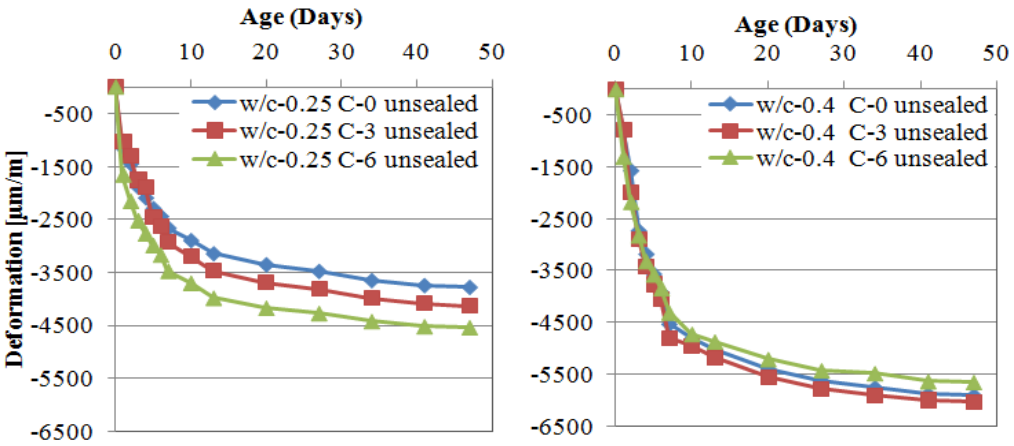
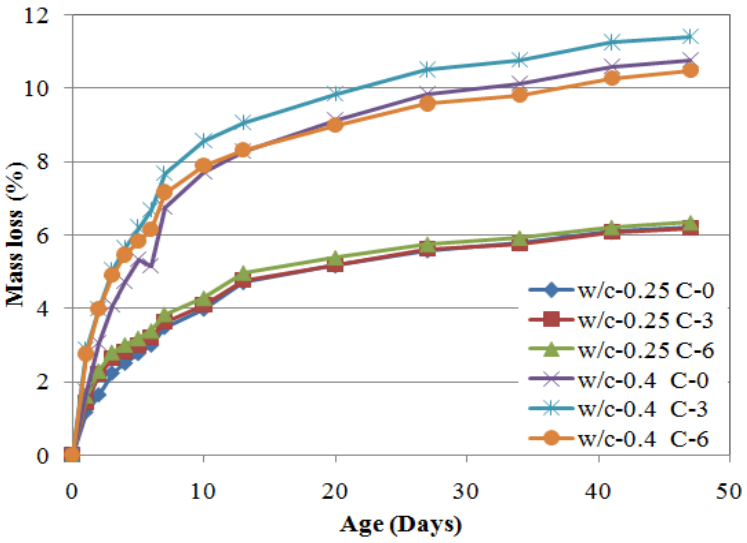


(a) (b)



(c)

Figure 4.9 Result for the dry shrinkage and mass loss

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4.4 Summary

In this chapter, a detail investigation on the hydration kinetics and shrinkage of a CNT composite cement matrix was analyzed by studying the microstructure property, rate of heat evolution, amount of bounded water, X-ray diffraction and linear deformation of the CNT composite material based on different time bases. Specimens without (0%) and with (0.3% & 0.6%) CNT have been analyzed in 0.25 and 0.4 water-cement ratio. From the experimental analysis, these four points have been made.

1. The result from the microstructure study of the paste matrix using MIP shows a slight increase in the total intruded volume of the paste matrix incorporated with CNT compared to the plain mixture results, which makes it difficult to state that if the CNT have any effect on the total volume of pores. In addition, the pore distribution graph shows a shift towards the mesopore in time from 3, 28 and to 91 days showing a slight shift for most of the CNT containing specimens than the plain samples and also the increase of the mesopore and decrease macropores intensity while shifting is observed. This might show the filler capability of CNT. However, the high surface area of the micro-level silica fume effect influences the microstructure properties highly by densifying the cement matrix more than the CNT making the effect of CNT negligible and difficult to be compared.

2. From the XRD analysis in general, the CNT shows no clear capability to activate the early age hydration in both water-cement ratio mixtures. However, in the long term, most of the CNT containing mixtures show an increase in hydration products. In addition, in this XRD analysis, there is no new peak observed for the CNT containing mixtures rather than the one observed in the plain mixtures, which shows that the CNT act as only a filler material.

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3. The isothermal calorimeter was conducted to verify the CNT capability to activate the hydration, which was seen in the XRD. From the result, it was not verified that the CNT have any capability to activate the hydration product at early ages. In addition, while the amount of the CNT content increase in the mixture a slight decreasing effect were observed in the hydration products for both water-cement ratio mixtures even though the difference was not significant.

4. Bounded water measurement to estimate the degree of hydration shows a different result compared to the XRD. From the measurement except for 0.4 water-cement ratio with 0.3% CNT, the remaining mixtures containing CNT for both water-cement ratios show a decrease in degree of hydration. In addition, from the experiment, the increase in CNT will decrease the degree of hydration as shown in the isothermal calorimeter even if it was a slight change.

5. The measurement of linear deformation for the autogenous shrinkage and dry shrinkage show a similar result, almost all CNT containing specimens show an increase in shrinkage. The shrinkage result shows that there is no enough water to fill the Capillary pores due to the further hydration of CNT containing mixtures as shown in the XRD. In addition, the results from the mass loss and microstructure properties also support the linear shrinkage results.

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Chapter 5. Conclusions

5.1Summary

The Nanoscale science research in the construction industry is currently growing. In this Research, a detailed study is made on the effect of the nano-filament, Multiwalled Carbon Nanotube (MWCNT), aiming to investigate its effect on the hydration kinetics and engineering properties. In addition, this study tries to look at the mechanism of the MWCNT on how it affects the flowability, shrinkage, mechanical property and hydration product formation on experimental and theoretical bases. Even though there is a significant amount of researches on the mechanical property enhancement of CNT. On the other hand, limited researches had only been carried out in analyzing the effect on shrinkage and hydration kinetics that makes this research characteristic. The other major difference in this research is that most of the researches used a physical and chemical method of desperation, mostly sonication, surfactant & functionalization that have an adverse effect on the mechanical and electrical property of the CNT besides affecting the cement matrix hydration in general. On the other hand, in this study, a micro-level silica fume was used to disperse the CNT mechanically through the cement matrix. Generally, the main objectives of this research are to show the effect of pure- CNT by mechanical desperation, on the mechanical property and on the shrinkage and hydration kinetics property to fill the Knowledge gap.

The study was performed in two parts; one is in analyzing the effect of the CNT on the Engineering property of the composite cement paste matrix such as flowability, compressive strength, flexural strength, and dynamic modulus. The other is by investigating the effect on the shrinkage and hydration kinetics by analyzing data's from, linear deformation, isothermal calorimeter, degree of hydration measurement. In addition, supporting experiments in order to reason out more were carried out such as Fourier transform infrared spectroscopy (FT-IR), mercury intrusion porosimetry (MIP) and X-ray powder diffraction (XRD).

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In general, from the experimental result except for compressive strength, the mechanical properties show an increase by incorporating CNT in the cement matrix. However, the addition of CNT led an increase in shrinkage and the degree of hydration was not changed by the use of CNT.

5.2 Limitations

In this study, one of the basic things to know where the physical properties of the CNT used in the experiment such as the length and aspect ratio which helps to specify the study in a further specific point. All most all the mechanical measurement was conducted on the same specimens' one after the other that may affect the experimental result output in addition to its small dimensions. Especially the compressive strength measurement that was taken after flexural measurement might be affected by the internal structure disturbance during the flexural test even though; there is a correction factor in the standard. The Flexural strength measurement that highly depends on the moisture condition of the specimen during measurement can be affected while measuring the young's modulus prior to the flexural measurement. However, note that for all specimens the same conditions were given while conducting the experiment. In addition, the measurement technique used, center point bending, for flexural measurement have a limitation on considering a constant moment, in other words, it is affected by shear effect during the test.

The other limitation in this research was the lack of mold with a small size (1mm x 1mmx 1mm) in the market for MIP measurement. Lack of the relative humidity measurement on the shrinkage specimens limits our understanding of the shrinkage result relative to the humidity effect. In addition, the lack of easy quantification methods for the crystalline and amorphous

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phase compounds in the XRD-pattern has impacted the study while comparing small range differences from a diagram.

5.3 Further studies

A detail study should be done on the effect of the different CNT physical properties in the paste matrix so, that it can be easily correlated, each physical properties of the CNT to that of correlating mechanical property effects. In addition, there is a lack of adequate theoretical explanation and prediction models on how the CNT, increase or decrease the mechanical properties include the shrinkage properties.

While conducting this study care was taken in order not to affect the electrical property of the CNT. However, further researches have to be carried out to investigate the electrical property of the cement matrix. Although the shrinkage was evaluated experimentally to increase while CNT combined with cement matrix but the main factor for the increase is still unknown in this study and open for further research. In addition, some results in the MIP during microstructure study put the MIP measurement in doubt, of its capability to analyze the dense pore structures of the cement pastes that needs also a further research for confirmation.

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