EFFECT OF MULTI-WALLED CARBON NANOTUBES AND SURFACTANTS TOWARDS MICRO-CRACK USING ACOUSTIC EMISSION TECHNIQUE

by

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LIST OF ABBREVIATIONS

AE: Acoustic Emission
A-FQR: average frequency
CMF: Carbon micro-fibre
CNF: Carbon nanofibre
CNT: Carbon nanotube
FRC: Fibre reinforced cement
MWCNTs: Multi walled carbon nanotubes
NDT: Non-Destructive Technique
RC: Reinforced cement
FESEM: Field Emission Scanning electron microscope
SHM: Structural Health Monitoring
SWCNT: Single walled carbon nanotube
TEM: Transmission electron microscope
TOA: Time of Arrival
UV-vis: Ultraviolet-visible spectroscopy
wt%: Weight percentage
C: Cement
C-S-H: Calcium Silicate Hydrates
HDT: Hit definition time
PDT: Peak definition time
HLT: Hit lockout time
W/C: Water to cement ratio
C/S: Cement to sand ratio

GLOSSARY AND TERMINOLOGY

Acoustic Emission (AE): the class of phenomena whereby transient elastic waves are generated by the rapid release of energy from localized sources within a material, or the transient waves so generated.

AE RMS: the rectified, time averaged AE signal, measured on a linear scale and reported in volts.

Attenuation: the decrease in ae amplitude per unit distance, normally expressed in dB per unit length.

Count: the number of times the acoustic emission signal exceeds a preset threshold during any selected portion of a test.

Effective Velocity: velocity calculated on the basis of arrival times and propagation distances determined by artificial ae generation; used for computed location.

Energy: the energy contained in an acoustic emission signal, which is evaluated as the integral of the volt-squared function over time.

Floating Threshold: any threshold with amplitude established by a time average measure of the input signal.

Hit: the detection and measurement of an ae signal on a channel.

Sensor: a detection device, generally piezoelectric, that transforms the particle motion produced by an elastic wave into an electrical signal.

Signal Strength: the measured area of the rectified ae signal with units proportional to volt-sec.

KESAN NANOTUBES KULIT MULTI-WALLED DAN KURSUS MENGURANGKAN MICRO-CRACK MENGGUNAKAN TEKNIQIK EMISI ACOUSTIK

ABSTRAK

Pertumbuhan dan pengumpulan mikro-retak yang membolehkan penembusan air dan kimia yang merosakkan ke matriks simen. Oleh itu, adalah penting untuk mengehadkan perkembangan peringkat awal dan apabila ia diperluaskan kepada ketahanan struktur konkrit. Kajian ini bertujuan untuk menyiasat jenis surfaktan pada penyebaran nanotube karbon berbilang berpandukan (MWCNTs) serta pengaruh kepekatan MWCNT yang berbeza terhadap sifat mekanik dan mekanik mortar simen serta pertumbuhan mikro dalaman mikro- retak dalam mortar simen MWCNT menggunakan teknik pelepasan akustik (AE). Ujian mekanikal yang berbeza termasuk ujian aliran, ujian ultrasonik, ujian pencirian ujian mampatan dan fleksibel seperti spektroskopi yang kelihatan UV, Mikroskop Elektronik Pengimbasan Pelepasan Medan (FESEM) dan Mikroskop Elektron Transmisi (HRTEM) telah digunakan untuk menilai sifat-sifat MWCNT- komposit simen. Teknik ini digunakan untuk mengesahkan prestasi mekanikal dan pertumbuhan retak mikro secara berasingan dalam mortar simen MWCN. Ujian pencirian menunjukkan kestabilan dan kestabilan yang memuaskan untuk surfaktan yang digunakan. Hasil ujian mekanik menunjukkan peningkatan yang signifikan dalam kekuatan mampatan dan sifat lentur mortar simen yang diperkuat dengan MWCNTs. Selain itu, pemerhatian mikrostruktur mortar simen MWCN menunjukkan bahawa MWCNT berkesan merapatkan keretakan mikro dalam matriks simen. Di samping itu, analisis AE mengesahkan bahawa MW boleh mengehadkan permulaan keretakan mikro dan melambatkan penyebaran dan pertumbuhan retakan mikro.

EFFECT OF MULTI-WALLED CARBON NANOTUBES AND SURFACTANTS TOWARDS MICRO-CRACK USING ACOUSTIC EMISSION TECHNIQUE

ABSTRACT

Growth and accumulation of micro-cracks result in formation of cracks at macro scale which allow penetration of water and deleterious chemicals to the cement matrix. Hence, it is essential to limit the development of cracks at the early stages and once they are at micro-scale to extend the durability of concrete structures. This study aims to investigate the effect of various types surfactant on dispersion of Multi-walled carbon nanotubes (MWCNTs) as well as the influence of different concentrations of MWCNTs on the engineering and mechanical properties of cement mortar as well as the growth of internal micro-cracks in MWCNT-cement mortar using acoustic emission (AE) technique. Different mechanical tests including flow test, ultrasonic test, compressive and flexural test as well as characterization test such as UV-visible spectroscopy, Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscopy (HRTEM) were employed to evaluate the properties of MWCNT-cement composites. In addition, AE technique was used to independently validate the mechanical performance and growth of micro-cracks in the MWCNT-cement mortar. The characterization tests showed a satisfactory level of dispersion and stability for the used surfactants. The results of mechanical tests showed significant improvements in compressive strength and flexural properties of cement mortars reinforced with MWCNTs. Moreover, the microstructure observation of MWCNT-cement mortars demonstrated that MWCNTs effectively bridging micro-cracks within the cement matrix. Besides, the AE analysis confirmed that MWCNTs can limit the initiation of micro-cracks and delay the propagation and growth of micro-cracks.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Cement composites, including cement paste, mortar and concrete, are the most commonly used construction material in the world (Gartner and Macphee, 2011). Aggressive development of infrastructures using cementitious materials is responsible for approximately one-third of global carbon dioxide (CO_2) emission, which is a serious concern in the current context of climate change and is worsening as the demand for cementitious materials expands (Allwood et al., 2011). Moreover, the brittle nature of cement (very low tensile strength and strain capacity) results in less durability and, consequently, frequent conservation operations (Pacheco-Torgal et al., 2013). Hence, degradation of concrete structures is a crucial issue all around the world. For instance, approximately 27% of all highway bridges in the United States and approximately 84,000 concrete bridges in the European Union require repair, rehabilitation or replacement (Peris Mora, 2007). Surely, enhancement of the mechanical properties of cement composite would lead to high durability and consequently, much less consumption of cement and energy. Hence, the control of cracking in concrete structures is very much desirable to satisfy durability and extending of structural life (Aldahdooh et al., 2013a).

Various factors are contributing to the deterioration of cementitious materials and concrete structures, but cracking is among the major causes of concrete deterioration. Cracking especially in chemical and environmental conditions accelerates deterioration of concrete structure and would significantly reduce the durability of concrete structures. Crack formation can be caused by different reasons such as shrinkage, chemical attacks, creep, fatigue or stress. The damage and fracture of concrete is a continuous process which starts from initiation and propagation of micro-cracks. Growth and accumulation of micro-cracks together result in the formation of the cracks in macroscale in structural members (Kabir et al., 2009). Macro-cracks provide a path for water and ionic species to penetrate the cement matrix which result in degradation of the cement matrix and the steel bars in the concrete. Hence, it is necessary to prevent the growth of nano and micro cracks in quasi-brittle materials like concrete from initial stages (Herrmann, 1991; Sagar and Prasad, 2011b).

Adding fibres to cementitious materials not only give mechanical strength but also can control cracking in the cement matrix. In the recent decades, a huge number of studies have been done on fibre-reinforced cement to enhance the properties of concrete composites by addition of various type and sizes of fibres (macro- to micro-scale). It has been shown that fibres limit the breakage of the brittle matrix and improve its weak tensile properties (Stähli and Van Mier, 2007). Corporation of fibres increase tensile strength and toughness of cement composites, as well as its ductility (Mobasher et al., 1990; Sivakumar and Santhanam, 2007). Moreover, fibres in the path of propagating cracks bridge the crack opening and resist further crack development (Aggelis et al., 2012). However, the utilization of fibre reinforcement in cementitious materials keeps on extending. Steel fibre, as the most common macro fibre, can stop development of macro cracks in cement composites but it cannot prevent the generation and growth of nano and micro and cracks. Recent research on nano-fibre reinforced composites has drawn out the promising outcomes such postponement on nucleation and development of cracks at the micro scale. Among the nano-materials and nano-fibres, multi-walled carbon nanotubes (MWCNTs) have demonstrated the most encouraging part to improve the properties of the cementitious materials and concrete (Peyvandi et al., 2014). MWCNTs can improve the ductility of the material due to their energy absorption capacity. Moreover, MWCNTs can control the nano and micro-cracks by preventing the micro cracks from widening and propagating. MWCNTs can enhance the flexibility of the material and keep the small-scale breaks from engendering or enlarging and help to control the nano and smaller scale splits. This property bridges the nano and micro-scale cracks inside the cement matrix and limit them from extending and development. Consequently, incorporation of MWCNTs as nano-fibres open a new field for reinforcement of cementitious materials (Sasmal et al., 2013; Sindu et al., 2014).

Figure 1-1 exhibits the relation of particle size and specific surface area identified with concrete materials (Sobolev and Gutiérrez, 2005). The ratio of particles surface and volume for spherical and fibrous particles as a function of the particle diameter is demonstrated in Figure 1-2 (Fiedler et al., 2006).

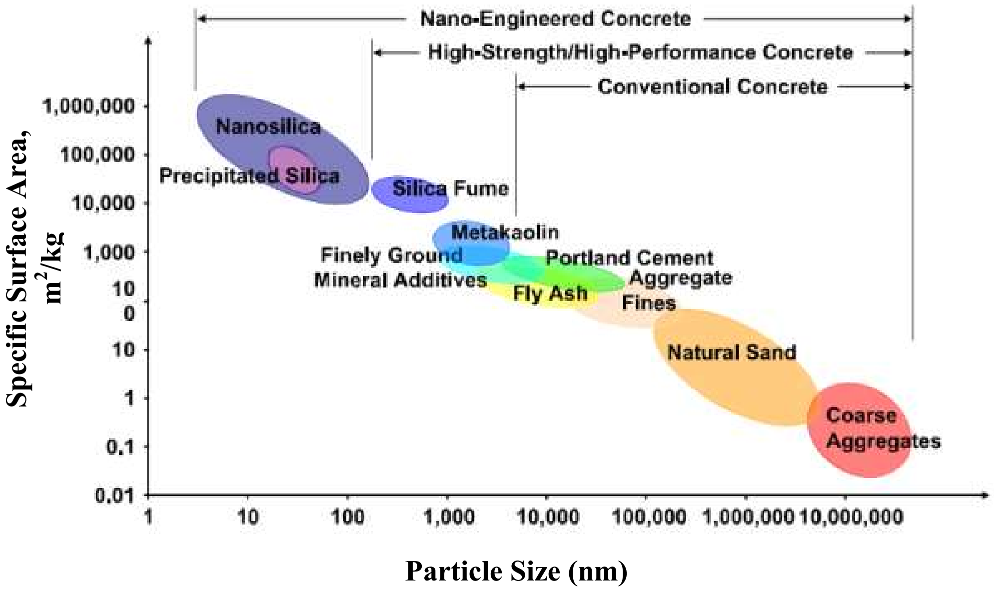

Figure 1-1. Relation of particle size and specific surface area identified with concrete materials (Sobolev and Gutiérrez, 2005)

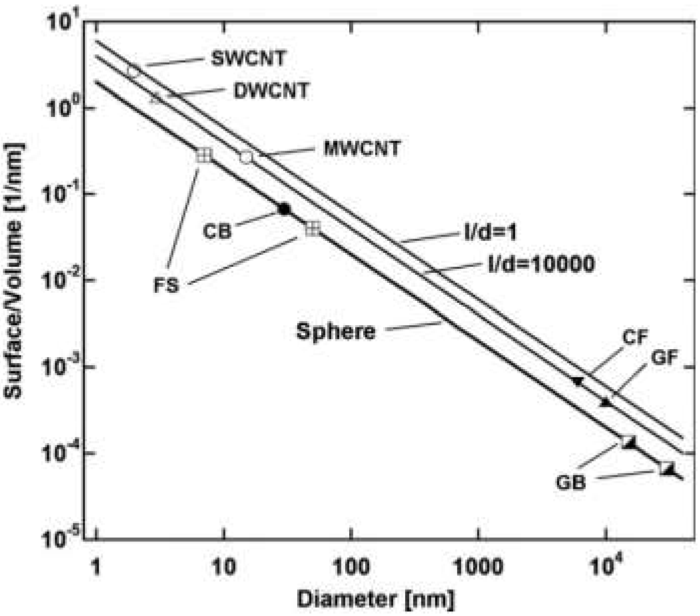

Figure 1-2. Ratio of particles surface and volume for spherical and fibrous particles as a function of the particle diameter (Fiedler et al., 2006)

Acoustic emission (AE) technique is a real-time inspection method which has been widely used in various fields including damage characterization of concrete structures (Gołaski et al., 2006; Shah and Weiss, 2006; Shiotani and Aggelis, 2007; Aggelis et al., 2008; Muhamad Bunnori, 2008; Bunnori et al., 2011; Shahidan et al., 2013). AE technique is the only possible approach to detect and investigate the internal micro-cracking in the materials. Investigation of the AE behaviour can prompt the characterization and evaluation of the damage level by means of the utilization of AE descriptors and subsequently gives an early cautioning before the macroscopic fracture. Moreover, the source of the AE events is associated with the mode of fracture. For instance, nucleation of shear cracks takes after tensile crack nucleation (Yuyama et al., 1999). On the other hand, the use of AE to characterise the behaviour of materials involves certain challenges. These mostly concern the accurate interpretation of the outcomes because of the distinctive individual procedures that contribute to the fracture of concrete. Fracture happens between various interfaces; cement paste and sand, mortar and aggregates, cement matrix and filaments as well as fibre rupture (Kumar and Gupta, 1996). In terms of size cracking can be classified into two major categories which are micro-cracking and macro-cracking. The micro-cracking formation and development is the first stage of fracture process of fibre reinforced concrete (Kabir et al., 2009). The AE technique can be utilized to characterize structural damage during the bending. In fact, the behaviour evolution of the composite is correlated with the evolution of the AE cumulative energy (Bravo et al., 2013). The AE signal parameters including AE activity (hits) and Energy were found to be very useful in evaluating the micro-cracking. This research aims to extend the knowledge of incorporation of multi-walled carbon nanotubes (MWCNTs) in cement composites and its effect on growth of micro-cracks in cement mortar.

1.2 Problem Statement

Durability and service-life of concrete structures is a derivative of cracking in cement matrix. Cementitious materials are quasi-brittle and susceptible to cracking and deterioration of concrete structures originates from initiation and development of cracks in cement matrix. In fact, growth and accumulation of micro-cracks result in formation of cracks at the macro-scale level. The macro-cracks allow water and deleterious chemicals to penetrate cement matrix which result in degradation of the cement matrix and the steel bars in the concrete. Hence, it is essential to limit the growth of micro-cracks in the cement composites at the early stages and once they are micro-scale. The best ways to mitigate the degradation of cement composites is to limit the amount of water that can penetrate through the matrix by minimizing the size of the cracks. Permeability of cement composites is proportional to the cube of crack width. Hence, from a durability perspective, it is preferable to have nano and micro-cracks in the cement matrix rather than macro-cracks (Kim, 1987; Hogancamp and Grasley, 2017).

One of the most effective approach to minimize the crack size is incorporation of fibres such as steel fibre, glass fibre and carbon fibre in the concrete and cement composites (Chung, 2001; Chaipanich et al., 2010b). Aveston and Kelly (1973) indicated that the size and the spacing between cracks are directly proportional to the diameter of the fibre used in the cement matrix. In the other words, fibres with smaller diameters produce more but smaller cracks in the material which is more desirable (Hogancamp and Grasley, 2017). Therefore, the use of nano-fibres in cementitious composites would result in nano and micro-cracks in the matrix. Moreover, it has been well known that fibres contribute to improving of mechanical properties of cement composites. Therefore, modification and reinforcement of cement composite using nano-fibres not only would increase the durability of cementitious materials but also can improve engineering and mechanical properties of concrete. On the other hand, demand for smart construction materials and multi-functional concrete is increasing in the construction section. Self-cleaning concretes have reached the markets and many other advanced features such as self-healing and self-sensing are under investigation. Therefore, incorporation of nanomaterials like MWCNTs can play a promising role toward development of multi-functional and smart concrete.

Many investigations have been carried out to develop the incorporation of MWCNTs in cement composites. However, there are still some challenges and questions that need to be addressed. Some obstacles such as homogenous dispersion of MWCNTs in the cement matrix as well as the bonding between MWCNTs and the cement matrix can be addressed. Indeed, the van der Waals' forces between CNTs and the high hydrophobicity of nanotubes make their dispersion a significant challenge. Moreover, the interfacial interaction between MWCNTs and the cement matrix is naturally weak such that individual MWCNTs tend to pull out when subjected to mechanical load. In addition, there are still many open questions that need to be answered. For instance, how do the concentrations of MWCNTs influence the properties of the MWCNT-cement composite? Among suggested approaches for dispersion of MWCNTs, which method is propitious for cement composites? What is the impact of dispersion techniques on the MWCNTs properties? Add to this, limited studies have been carried out to investigate the influence of superplasticisers as surfactant compatible with cement products on dispersion of MWCNTs. Moreover, no study has been conducted on the corporation of MWCNTs as nano-fibres on growth of micro-cracks in cement mortar.

However, the microstructure observation of MWCNT-cement composites demonstrate a detailed geometry of micro-cracking, FESEM images do not represent the whole area of the matrix and the overall performance of the composite. Moreover such observation is very sophisticated and costly. Hence AE technique is a real-time inspection method and the only possible technique to detect the internal micro-cracking in the materials can be used for monitoring and evolution of micro-cracking in the cement matrix.

1.3 Research Objectives

The focus of this study is to develop the incorporation of MWCNTs as nano-fibres in cement composites to enhance the durability of cementitious materials as well as development of MWCNT-cement mortar as a multi-functional cementitious composite. For this purpose, the following objectives needs to be addressed:

a) To characterize the effect of various types of surfactant and sonication technique on dispersion of MWCNTs within the aqueous solution and within the cement matrix.

b) To investigate the mechanical properties of the cement mortar reinforced with MWCNTs at different concentration

c) To investigate the microstructural of MWCNT-cement composites.

d) To assess the effect of MWCNTs reinforcement on growth and development of micro-cracks within the cement matrix using AE technique.

1.4 Structure of Thesis

This thesis comprises of six chapters. Chapter One presents the introduction, problem statement and objectives of this study.

Chapter Two presents a background on fibre reinforced cement-base materials. Then an introduction to properties of MWCNTs and challenges in the area of application of nanotubes in cementitious materials are presented. The chapter is followed by an introduction to theory of acoustic emission (AE) technique.

Chapter Three presents the research methodology including the approach proposed for dispersion of MWCNTs, mixing as well as samples preparation process. Experimental setups for mechanical and characterization tests are also explained in this chapter. Afterward, experimental set up for AE monitoring procedure is explained.

In Chapter Four, the approaches applied for dispersion of MWCNTs is evaluated and discussed. In addition, the engineering and mechanical properties of MWCNT-cement composite are investigated. Following, MWCNT-cement composites are characterized and the results from characterization tests are discussed.

Chapter Five presents and discuss the finding and results of AE monitoring from MWCNT-cement composite during bending test.

Chapter Six presents the general conclusions and discoveries of this research study. Moreover, some recommendation for future work is presented.

CHAPTER TWO

LITERATURE REVIEW

This chapter consists of two main sections; the first section provides a background of fibre reinforced cement-based composite and general overview of properties of multi-walled carbon nanotubes (MWCNTs). In addition, challenges and ways forward for developing of MWCNT-cement mortar is reviewed. The second section provides an overview of application of Acoustic Emission (AE) technique for monitoring and crack assessment in concrete.

2.1 Fibre Reinforced Cement-Based Composites

It has been well known that properties of cement composites can be improved by incorporation of fibres. Fibres restrain the breakage of the brittle matrix and enhance its weak tensile properties Stähli and Van Mier (2007). Fibres contribute to improve concrete tensile and flexural strength, fatigue life and ductility and toughness (Mobasher et al., 1990; Sivakumar and Santhanam, 2007). The application of fibre reinforcement in cementitious materials continues to expand.

Nanotechnology has provided tremendous opportunities for engineers to enhance the properties of materials and furthermore to conquer numerous perennial limitations of conventional materials (Sanchez and Sobolev, 2010). Recently, carbon-based nano-structural materials, such as fullerene, carbon nano-fibres and carbon nanotubes, have demonstrated remarkable potential for producing new generation of nano-fibre reinforced composites (Sindu et al., 2014). Among the nano-fibres, MWCNTs have garnered the most interest from researchers due to their vast surface area and high aspect ratio and strength. Fibres typically have an aspect ratio (length/diameter) of less than 300 (Zollo, 1997; Metaxa et al., 2017); however, carbon nanotubes with aspect ratios of 1000 - 2500000 and surface areas of approximately 300 m^2/g can result in a vast bond area for the reinforcement of cement composites. In fact, the aspect ratio and surface area of fibres are crucial factors in providing the best and most efficient fibre-reinforced composite material (Shah et al., 2009; Ashour, 2011b; Noiseux-Lauze and Akhras, 2013; Wang et al., 2013). Table 2-1 presents a comparison between the mechanical properties of carbon nanotubes and other types of fibre.

Table 2-1. Comparison of the mechanical properties of MWCNT and other fibres (Salvetat et al., 1999; Yu et al., 2000; Chaipanich et al., 2010b; Kim et al., 2014b; Siddique and Mehta, 2014)

Fibre Type	**Diameter (µm)**	**Young Modulus (GPa)**	**Tensile Strength (GPa)**	**Yield Strain (%)**
Carbon Nanotube	0.001-0.05	500-5000	30-200	10-23
Carbon Fibre	5-15	230-600	1.1-6	0.5-10
Glass Fibre	6-21	72-80	1.5-4.7	2.5-4.8
Steel Fibre	400-800	200	0.5-2.6	0.5-3.5

2.1.1 MWCNT-cementitious Composites

To exhibit remarkable and potential properties of MWCNT-cement composites, there are two significant issues that need to be addressed: (i) homogenous dispersion of MWCNTs in the cement matrix and (ii) strong bonding between MWCNTs and the cement matrix. Indeed, the van der Waals' forces between MWCNTs and the high hydrophobicity of nanotubes make their dispersion a significant challenge (Fraga et al., 2014). Moreover, the interfacial interaction between MWCNTs and the cement matrix is naturally weak such that individual MWCNTs tend to pull out when subjected to mechanical load (Kim et al., 2014b). In addition, advances in synthesis techniques and successful research into large-scale production of MWCNTs, as well as increased demand for its mass production, are diminishing its cost very quickly which makes the utilization of MWCNTs in the construction industry more practical. For example, the cost of industrial MWCNTs has decreased from $1200/kg in 2006 to less than $100/kg in 2016 (Noiseux-Lauze and Akhras, 2013; Fraga et al., 2014).

Many investigations have been carried out to surmount these obstacles, but there are still many open questions that need to be addressed (Sobolkina et al., 2012, Kim et al. 2014b, Lu et al., 2015, Sun et al., 2016, Gdoutos et al. Gdoutos, 2016). For instance, how do the properties, type and concentration of MWCNTs influence the properties of the MWCNT-cement composite? What is the impact of sonication parameters on the MWCNTs properties and how can structural damage and degradation of MWCNTs during the sonication process be avoided? Among suggested chemical approaches for the treatment of MWCNTs, which methods are propitious for cement composites? Moreover, the influence of chemical treatment on cement hydration still needs to be clarified. Furthermore, the optimum MWCNT-to-surfactant ratio for different types of surfactants should be determined. Finally, there is little knowledge regarding the bonding of MWCNTs and the cement matrix, and there have so far been no systematic investigations of this issue.

This research study aims to address a portion of the previously mentioned inquiries regarding developing the MWCNT-cement composites. The focus would be on the effect of MWCNTs on the mechanical properties of cement-based composites and the characterization of their microstructure.

2.1.2 An Overview of the Properties of Carbon Nanotubes

Many theoretical and experimental have been done to examine the properties of nanotubes since their revelation by Iijima (1991). Carbon nanotubes have received much attention for their unique structure and mechanical, chemical, electrical and thermal properties. To make use of MWCNTs in cement composites, it is indeed necessary to know the structural features and mechanical properties of the carbon nanotubes. The following sections presents a review on structure and properties of carbon nanotube.

2.1.2(a) Structure and Geometry

A carbon nanotube is made of a graphene sheet rolled into a seamless cylinder. Graphene is a level sheet framed by carbon particle layers reinforced in a hexagonal pattern. Carbon nanotube (CNTs) are arranged as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). An SWCNT is made of a single graphene sheet, while a MWCNT is composed of two or more graphene sheets, as illustrated in Figure 2-1 (a and b), respectively (Vidu et al., 2014). In other words, a MWCNT consists of concentric SWCNTs coaxially arranged around a central hollow area.

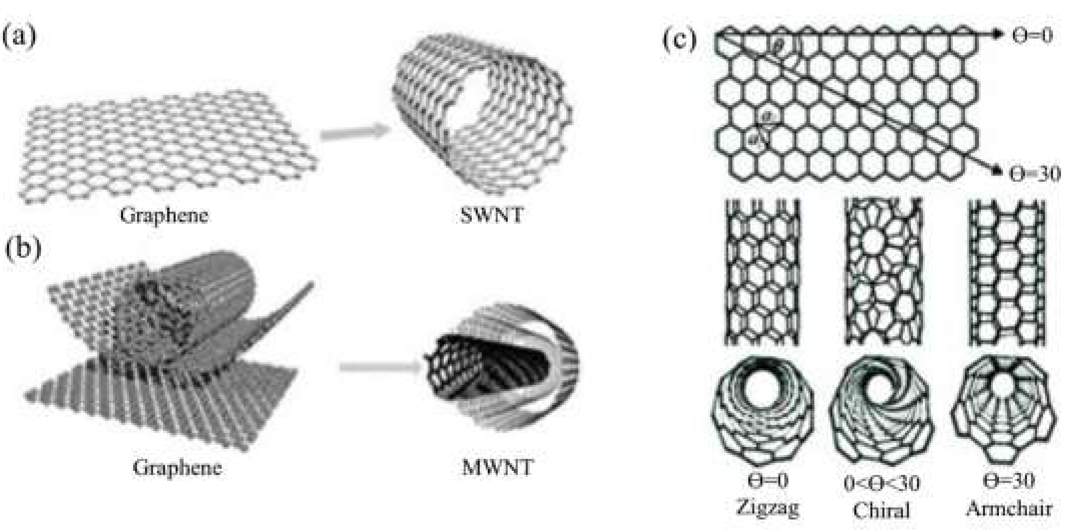

Figure 2-1. Graphene sheets rolled into nanotubes (a) SWCNT and (b) MWCNT (Vidu et al., 2014) and (c) different chiralities of carbon nanotubes (Galano, 2010)

In a graphene sheet, the atomic structure of nanotubes is defined by the tube chirality. In light of the way the graphene sheet is moved to shape the CNT, three major chiralites of a CNT, i.e., zig-zag-shaped (chiral angle of 0°), Chiral (chiral angle between 0°-30°) and armchair-shaped (chiral angle of 30°), are formed (Qian et al., 2002; Sasmal et al., 2013). The major chiralites of CNTs are shown in Figure 2-1 (c).

2.1.2(b) Synthesis Methods

The nanostructure, geometry and properties of a nanotube highly depend upon the production method and growth parameters (Collins and Avouris, 2000). Because the initial synthesis and discovery of nanotubes using arc discharge method, different techniques, such as laser ablation, hydrocarbon flames and chemical vapour deposition (CVD), have been developed to produce MWCNTs. Among the synthesis methods, CVD is the most well-known for industrial (modern)-scale production due to its value as well as the fact that it grows nanotubes directly on a desired substrate, which removes the collection process (Sethi, 2014). In the CVD technique, the structure of synthesized MWCNTs can be controlled by growth parameters to have higher yield, purity and quality (Musso et al., 2009; Khavarian et al., 2013). MWCNTs synthesised by CVD have a larger amount of lattice defects along the graphene walls, which degrade to some extent the properties of MWCNTs. Moreover, an issue in the catalytic CVD system is the expulsion of the residual catalyst particles through acid treatment, which can infrequently destroy the initial structure of the nanotubes. However, these surface defects provide reactive sites for functionalization of MWCNTs (Campillo et al., 2004). Figure 2-2 is a schematic representation of MWCNTs synthesis methods (Gore and Sane, 2011) and the MWCNTs growth model (Khavarian et al., 2010).

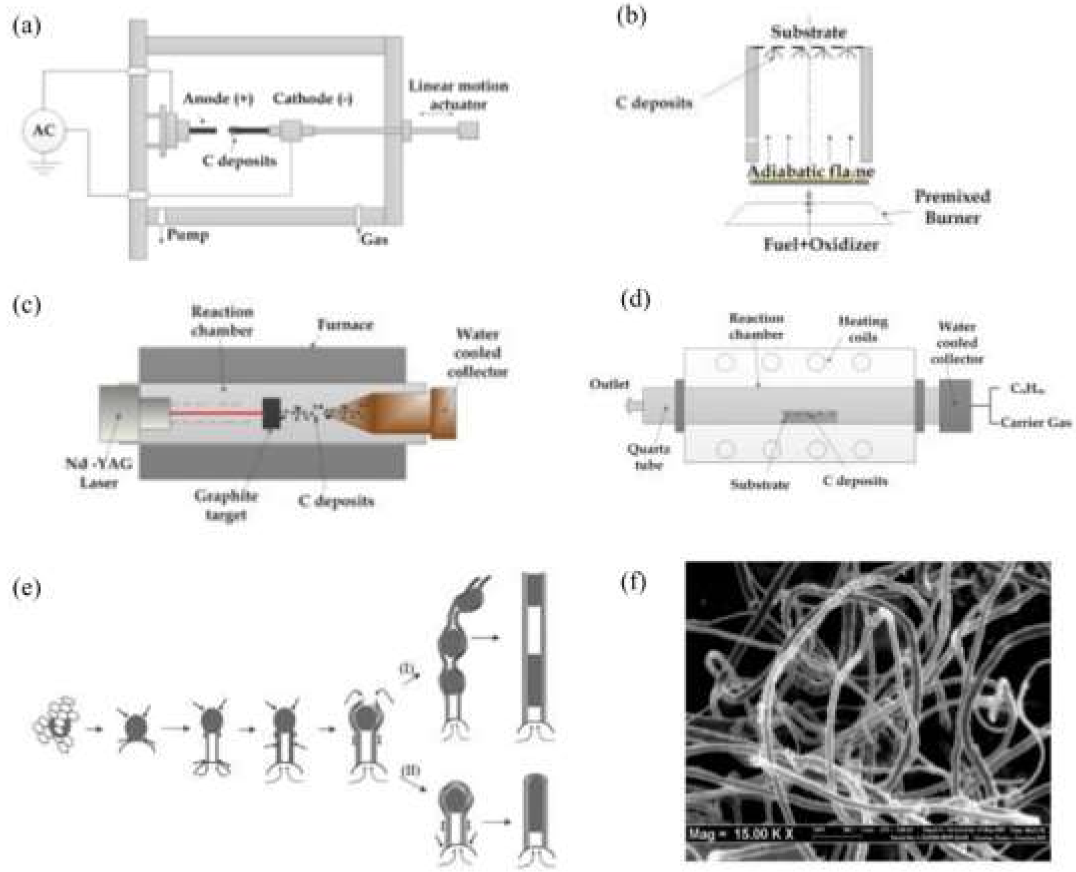

Figure 2-2. Schematic representation of methods used for carbon nanotube synthesis (a) arc discharge, (b) hydrocarbon flames, (c) laser ablation, (d) chemical vapour deposition (CVD) (Gore and Sane 2011), (e) model of carbon nanotube growth (Khavarian et al., 2013) and (f) FESEM micrograph of a bundle of MWCNTs produced by CVD technique from camphor and ferrocene (Khavarian et al., 2010)

2.1.2(c) Physical and Mechanical Properties

The properties of MWCNTs hinge upon their structure (the atomic arrangement of carbon atoms) and geometry (diameter and chirality) (Yu et al., 2000; Wansom et al., 2006). For example, in terms of electrical properties depending on the geometry of MWCNTs, it can be a conductor or semiconductor (Ebbesen, 1996). Typically, MWCNTs length varies from 0.5 to 50 µm. SWCNTs diameter ranges from less than one to a few nm, and for MWCNTs, it varies from 2 to 100 nm depending on number of walls in its structure (Liu et al., 2010). In MWCNTs, the internal spacing between walls is approximately 0.34 to 0.39 nm (Eatemadi et al., 2014). Sindu et al. (2014) determined the mechanical properties of different MWCNTs utilizing nanoscale continuum hypothesis and numerical simulation. They evaluated the impact of parameters such as the aspect ratio, chirality and radius of nanotubes on tensile stiffness and the Young’s modulus of MWCNTs. They found that the tensile stiffness of MWCNTs relies upon the chirality and radius of nanotubes and is nearly independent of its aspect ratio. Moreover, it was discovered that the tensile stiffness of the zigzag type is more prominent than the armchair type up to a radius of 0.8 nm, and beyond this radius, the tensile stiffness of a nanotube is not dependent on its chirality and radius. Figure 2-3 (a and b) shows the radius and aspect ratio versus tensile stiffness for armchair and zigzag CNTs, respectively (Sindu et al., 2014).

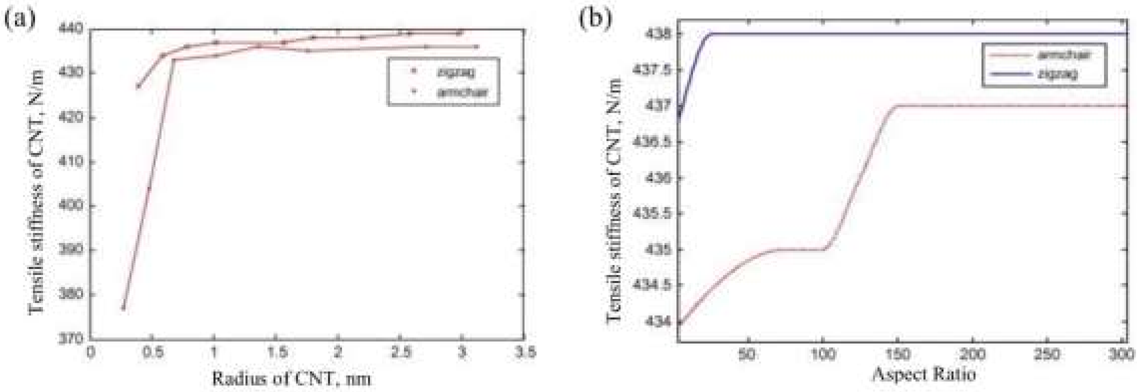

Figure 2-3. (a) Radius and (b) aspect ratio vs. tensile stiffness for armchair and zigzag CNTs (Sindu et al., 2014)

The structural perfection and strong covalent bonds (carbon-carbon bonds) make nanotubes the stiffest and strongest materials yet found in terms of modulus of elastic and tensile strength, respectively. For comparison, the Young's modulus of MWCNTs is approximately 3 TPa, and its tensile strength is approximately 100 GPa, while those values for high-strength steel are approximately 200 GPa and 2 GPa, respectively (Siddique and Mehta, 2014; Sindu et al., 2014). The tensile strength of MWCNTs is not as high as that of SWCNTs due to the weak shear interactions between tubes (Filleter et al., 2011). The hollow centre structure of a MWCNT makes it one-sixth the weight of copper and approximately half the weight of aluminium; however, the hollow structure and the high aspect ratio of MWCNTs lead to significant reductions in compression, torsion and bending stress (Qian et al., 2002). Moreover, MWCNTs have presented extraordinary thermal properties (stable until 2800°C in a vacuum) and electrical properties (conductivity 1000 times higher than that of copper) (Salvetat et al., 1999; Forro et al., 2002). Furthermore, MWCNTs are stable under extreme chemical environments, high temperatures and moisture. A comparison of mechanical properties of SWCNTs and MWCNTs is shown in Table 2-2.

Table 2-2. Comparison of mechanical properties of SWCNTs and MWCNTs (Salvetat et al., 1999; Yu et al., 2000).

Type	**Diameter (nm)**	**Aspect Ratio**	**Young's Modulus (GPa)**	**Tensile Strength (GPa)**	**Yield Strain (%)**
SWCNT	1- 3	100000 - 2500000	1000 - 5000	53 - 200	16 - 23
MWCNT	2 - 100	500 - 100000	200 - 950	11- 63	10

2.1.3 Challenges and Ways Forward for Developing MWCNT-Cement Composites

MWCNTs have been widely implemented in the reinforcement of different types of composites such as polymers, metals and ceramics, and has led to significant improvements in the mechanical properties of the composites (Fakhru'l-Razi et al., 2006; Uddin et al., 2010; Bi et al., 2013; Laurenzi et al., 2013; Wernik and Meguid, 2014; Yue et al., 2014; Saeb et al., 2015). However, limited studies have been performed on the incorporation of MWCNTs in cement composites (Coleman et al., 2006). Indeed, homogeneous dispersion and strong bonding are two primary factors for developing fibre-reinforced composites (Montazeri and Chitsazzadeh, 2014). Likewise, properties of the MWCNT-cement composite greatly rely upon the dispersion of MWCNTs in the composite and the bonding between nanotubes and the composite matrix. In fact, these two factors are the main challenges when MWCNTs are added to cement composites (Makar et al., 2005). Proposed approaches and some well-reported techniques towards developing MWCNT-cement composites are subsequently discussed.

2.1.4 Dispersion of MWCNTs in the Cement Matrix

As mentioned previously, one of the significant issues in the context of MWCNT-cement composite development is the dispersion of MWCNTs in the cement matrix. Dispersion means breaking up the agglomerated MWCNTs into individual nanotubes because the as-produced MWCNTs contain a large bundled network of rope-like structures (Bandyopadhyaya et al., 2001; Shah et al., 2009). Dispersion or exfoliation of bundled MWCNTs is almost impossible via simple mixing procedures due to the van der Waals' forces between MWCNTs as well as the hydrophobicity of nanotubes (Makar and Beaudoin, 2004b; Xie et al., 2005; Fraga et al., 2014). A variety of mechanical and chemical approaches has been proposed in previous studies and can be used in series or parallel to promote a uniform and stable dispersion.

2.1.4(a) Mechanical Dispersion

Mechanical approaches for dispersion of MWCNTs include calendaring, ball milling (Gojny et al., 2004), high shear mixing (Andrews et al., 2002; Luo et al., 2011a) and sonication (Cwirzen et al., 2008; Shah et al., 2009; Kumar et al., 2011; Abu Al-Rub et al., 2012; Sobolkina et al., 2012; Mohsen et al., 2017; Tolchkov et al., 2018). Sonication using a bath or probe is the most effective and common mechanical technique for the dispersion of MWCNTs, but a probe sonicator is more efficient for achieving a better dispersion (Vaisman et al., 2006; Cwirzen et al., 2008) (Wang et al., 2017a). In this technique, high-frequency acoustic energy is induced in a solution to transmit vibration waves to nanotube bundles and push them apart. The vibration waves lead to the formation of micro/nano-cavitation in the solution, and these vacuum bubbles implode by touching the surface of MWCNTs. The implosion causes a huge vacuum force that result in the separation of the nanotubes in the solution (Cwirzen et al., 2008; Kumar et al., 2011; Kim et al., 2014b). Many researchers have applied the sonication technique for the dispersion of MWCNTs, but only a few of them have evaluated the effect of sonication parameters on the dispersion and structure of MWCNTs. These parameters include the amplitude, intensity and time of sonication, as well as the viscosity, temperature and type of solution media(Dassios et al., 2015; Zou et al., 2015). It is noteworthy that the supplied energy should be optimized to be lower than the fracture resistance of individual nanotubes (upper limit) and greater than the binding energy (lower limit) because inadequate sonication power will not disperse nanotubes, and an excessive amount of energy breaks and degrades the structure of nanotubes, which is not desirable (Huang and Terentjev, 2012). Suave et al. (2009) investigated the effect of sonication duration and power on the dispersion of MWCNTs. They applied low and high power (165 and 225 W) for short and long periods of time (20 and 40 min) and observed that low-power sonication performed over a longer period of time resulted in better dispersion. Cwirzen et al. (2009a) used an ultrasonic processor for 2 min at 50 Hz for the dispersion of MWCNTs bundles in water. Noiseux-Lauze and Akhras (2013) used a magnetic stirrer and then sonicated the water-MWCNTs solution for 40 min (programmed on a pulse setting with 20 second on, 20 second off) to disperse the nanotubes. Kumar et al. (2011) evaluated the effect of sonication time (30 and 240 min) on the dispersion of different amounts of MWCNTs (0.5, 0.75 and 1 wt% by weight of cement). They found a better dispersion for the lower percentage of MWCNTs, but longer sonication time did not have any significant impact on the dispersion of MWCNTs. Luo et al. (2011a) and Luo et al. (2011b) applied sonication and high-speed shear mixing to disperse MWCNTs and investigate the incorporation of different concentrations of MWCNTs (0.1, 0.5 and 1 wt%) in silica fume-cement paste. Hunashyal et al. (2011) applied the sonication energy to disperse relatively high concentrations of MWCNTs (0.25, 0.5, 0.75, 1 wt%). They sonicated the MWCNTs solution for 90 min and then added the cement and sonicated it again for another 30 min. Chaipanich et al. (2010a) sonicated 0.5 and 1 wt% MWCNTs by weight of cement for 10 min and then added it to a cement mixture containing 20% fly ash to produce a MWCNTs-fly ash-cement composite.

Although water has been used as a common media for sonication solutions, other types of solvents, such as toluene (a non-polar solvent), ethanol and acetone (polar solvents), have been applied. For instance, Musso et al. (2009) sonicated the MWCNTs for 4 h in acetone and then allowed the acetone to evaporate. Makar and Beaudoin (2004a) sonicated MWCNTs in ethanol for 2 h and then for 5 h (after adding the cement powder) and finally evaporated the ethanol. The result indicated that the cement grains were covered by the MWCNTs; however, some changes were observed on the surface of the cement grains, probably due to sonication. In another attempt, Makar et al. (2005) investigated the dispersion of MWCNTs in hydrated and non-hydrated cement powder and observed that the level of dispersion was not the same in the hydrated and non-hydrated cement.

The size of the cementitious material plays a crucial role in the dispersion of MWCNTs; hence, application of extremely fine particles has been considered a mechanical approach for the dispersion of MWCNTs in cement composites (Chaipanich et al., 2010a). Silica fume, because of its extremely fine size (like the MWCNTs size and much smaller than cement particles), can promote good dispersion of MWCNTs in the cement matrix (Sanchez and Ince, 2009; Shah et al., 2009; Luo et al., 2011b; Kim et al., 2014b). Table 2-3 shows a comparison between the sizes of cementitious materials and MWCNTs. Kim et al. (2014a) applied different concentrations of silica fume (10%, 20% and 30%) in a cement composite and observed individual MWCNTs embedded in silica fume-cement hydration products. They also revealed that the amount of silica fume could influence the morphology of the MWCNTs which are dispersed in the matrix.

Table 2-3. Particle size of cementitious materials (Sanchez and Ince, 2009; Kim et al., 2014b; Sethi, 2014)

Particle	Particle Size (Typical) (μm)	Surface Area (m^2/kg)
Portland Cement	5-30	300-400
Fly Ash	1-20	400-700
Silica Fume	0.01-0.2	30000-130000
MWCNTs	0.001-0.05	300000-350000

In addition to the dispersion of MWCNTs in aqueous solutions, some researchers, such as Bharj (2015), Azhari and Banthia (2012) and Cui et al. (2015), used a dry mix method (mixing MWCNTs and cement powder) for the dispersion of MWCNTs. Cui et al. (2015) used a high-speed mixing method to disperse MWCNTs in the cement powder. They found that the dry mix method is not as effective as aqueous mixing; however, they suggested that a longer mixing time after adding water and surfactant might ensure uniform dispersion of MWCNTs in cement paste. Azhari and Banthia (2012) reported similar resistivity values for the samples produced from dry and aqueous mixing methods and concluded that both mixing methods provide the same level of dispersion.

2.1.4(b) Chemical Treatment

Mechanical exfoliation of MWCNT bundles through sonication or other mechanical techniques is essential for the dispersion of MWCNTs; however, the strong van der Waals’ forces between MWCNTs pull the nanotubes back together (Ashour, 2011b). Chemical treatment or surface modification is an effective approach to obtain a sustainable dispersion of MWCNTs. In addition, characteristics of MWCNTs can be adjusted to fit a specific application by applying a suitable chemical treatment. In general, chemical treatment (surface modification) methods can be categorized into covalent functionalization and noncovalent functionalization approaches, which are subsequently reviewed and analysed.

a) Non-Covalent Functionalization

The usage of surfactant is a non-covalent functionalization method that has been widely used to enhance the dispersion of MWCNTs. In this approach, a chemical agent absorbs at the interface of MWCNTs and the solution, without disturbing the surface of nanotubes, to reduce the surface tension and in this way keep the MWCNTs suspended and isolated inside the solution (Vaisman et al., 2006). Surfactants have a hydrophilic head and hydrophobic tail in their amphiphilic chemical structure, and the hydrophobic head is attracted to the surface of MWCNTs. Surfactants can be classified according to the head groups into anionic surfactants, such as Sodium Dodecyl Sulphate (SDS) (Han et al., 2011; Sobolkina et al., 2012; Siddique and Mehta, 2014) and Sodium Dodecyl Benzene Sulfonate (SDBS) (Yazdanbakhsh et al., 2009b), and non-ionic surfactants, such as polyoxyethylene and laurylether (Sobolkina et al., 2012).

Various types of surfactants and polymers have been implemented within different types of composites, but only a few of these surfactants are applicable to cementitious composites. In fact, incompatible surfactants may affect the chemical reactions or hardening process of cement by retarding or even stopping the hydration process of cement (Ashour, 2011b; Sasmal et al., 2013). Yazdanbakhsh et al. (2009b) proposed that SDBS hindered the initial setting of cement paste for 24 hours. Yu and Kwon (2009) dispersed MWCNTs with SDS to fabricate piezo-resistive MWCNTs cementitious composites, and they found that the excessive amount of SDS impairs cement hydration and causes a decrease in the mechanical properties of composites. Similar results have been reported by Sáez de Ibarra et al. (2006). Azhari and Banthia (2012) used methylcellulose as surfactant in MWCNT-cement composites and observed a degradation in the mechanical properties of composites, probably due to the air-entraining effect. Another dispersant agent that has been used as a surfactant is Arabic gum. Wang et al. (2012) and Wang et al. (2013) reported that Arabic gum it is not preferable for cementitious materials. They observed that application of Arabic gum delayed the cement hydration process; however, this delay did not affect the mechanical strength. Cwirzen et al. (2008) inferred that the incorporation of 0.8% Arabic gum could provide a good dispersion and workability.

Surfactants not only enhance the dispersion of MWCNTs but also reduce the amount of sonication power and time for dispersion. In other words, more surfactant means less energy; however, the surfactant-to-MWCNTs ratio should be optimized. In fact, an insufficient amount of surfactant may result in sedimentation of nanotubes during storage time, and conversely, an excessive amount of surfactant may affect the cement paste hydration process and delay the hydration process of cement or act as an air entraining agent that degrades the mechanical properties of composites (Sasmal et al., 2013; Kim et al., 2014b). Konsta-Gdoutos et al. (2010a) have investigated the effect of different surfactant-to-MWCNTs ratios on fracture load of cement paste as shown in Figure 2-4.