

Evaluation on mechanical enhancement and fire resistance of carbon nanotube (CNT) reinforced concrete

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Abstract. To cope with the demand on giant and durable buildings, reinforcement of concrete is a practical problem being extensively investigated in the civil engineering field. Among various reinforcing techniques, fiber-reinforced concrete (FRC) has been proven to be an effective approach. In practice, such fibers include steel fibers, polyvinyl alcohol (PVA) fibers, polyacrylonitrile (PAN) carbon fibers and asbestos fibers, with the length scale ranging from centimeters to micrometers. When advancing such technique down to the nanoscale, it is noticed that carbon nanotubes (CNTs) are stronger than other fibers and can provide a better reinforcement to concrete. In the last decade, CNT-reinforced concrete attracts a lot of attentions in research. Despite high cost of CNTs at present, the growing availability of carbon materials might push the usage of CNTs into practice in the near future, making the reinforcement technique of great potential. A review of existing research works may constitute a conclusive reference and facilitate further developments. In reference to the recent experimental works, this paper reports some key evaluations on CNT-reinforced cementitious materials, covering FRC mechanism, CNT dispersion, CNT-cement structures, mechanical properties and fire safety. Emphasis is placed on the interplay between CNTs and calcium silicate hydrate (C-S-H) at the nanoscale. The relationship between the CNTs-cement structures and the mechanical enhancement, especially at a high-temperature condition, is discussed based on molecular dynamics simulations. After concluding remarks, challenges to improve the CNTs reinforcement technique are proposed.

Keywords: carbon nanotube (CNT); fiber-reinforced concrete (FRC); mechanical properties; fire safety

1. Introduction

Concrete is a widely-used construction material in modern society. Reinforcement of concrete in terms of strength and durability has been long pursued in the civil engineering field, considering that a higher strength can improve reliability of concrete buildings and a better durability can reduce the cost for long-term maintenance. Incorporating other strong and durable materials is a common approach to reinforce concrete, where normally selected materials include steel, glass

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fiber and organic fibers. Those materials can be planted inside or attached to the surface of concrete structures, to achieve a direct mechanical reinforcement at the macroscopic scale. However, the macroscopic reinforcement faces the limitation originated from the microscopic cracks in concrete itself, regardless of how strong the reinforcing component is. Therefore, the key to the further enhancement of the concrete mechanical properties lies at the micro- as well as the nanoscale, where the addition of nanomaterials and even the astute reorganization of the molecular structures could internally improve the cement-based composite. Such small-scale engineering requires a systematic multi-scale understanding of concrete structures (Palkovic *et al.* 2016), which is introduced below.

Concrete is a heterogeneous material composed of aggregates and cement. It can be described as a solid dispersion of hard inclusions into a cohesive matrix, to which the hydrated cement provides the binding strength. In cement, the major cohesive hydration product is calcium silicate hydrate (C-S-H), which is a porous gel-like material generated from the hydration of crystalline mineral particles in Portland cement powder. Because the components are not perfectly bonded, pores and pre-cracks often exist in hardened concrete (Gangsa *et al.* 2015, Oesch *et al.* 2016). Many reinforcing techniques are based on nanofillers that fill the pores, connect the components and transfer stresses in concrete. Fiber-reinforced concrete (FRC) is a product out of this bridging concept. Fibers are added to the concrete aiming to bridge separated components for mechanical enhancement, especially at the post-cracking stage. Also, FRC can provide improved resistance against spalling at elevated temperature condition, permitting a high level of fire safety. Existing well-developed FRC techniques are based on fibers including but not limited to steel fiber, glass fiber, pitch carbon fiber, polypropylene, polyethylene, polyolefin and polyvinyl alcohol (PVA). Those fibers are within the length scale ranging from centimeters to micrometers but do not provide nanoscale reinforcement. Carbon nanotubes (CNTs), known for the elegant structure and superb material properties, are of great potential to be extensively dispersed into cement filling up the pores and modifying the structures at the nanoscale. Incorporation of CNTs into concrete is of great potential to improve the overall material properties including stiffness, tensile strength, compressive strength, conductance and functional properties. In practice, the method to achieve an adequately good dispersion of CNTs into the concrete system is an essential engineering problem to tackle. Currently, most experimental works and reviews are based the fabrication of the CNT-reinforced cement composite and the characterization the mechanical properties such as compressive strength. Discussions about microstructures, working principles of the dispersed CNTs as well as the fire safety are few. In order to gain a better understanding of the interplay between CNTs, C-S-H and resulted mechanical enhancement, a systematic evaluation on how the CNTs exist in the concrete system and how they bring about the mechanical enhancement is necessary. Up to now, a series of reviews of nanotechnology in concrete can be found (Han *et al.* 2015, Lee *et al.* 2010, Li *et al.* 2015, Mukhopadhyay 2011, Parveen *et al.* 2013, Sanchez and Sobolev 2010, Xie *et al.* 2005), with focus on dispersion methods, characterizing techniques, microstructures, mechanical improvements, multifunctional properties and potential engineering applications. Multi-scale modeling techniques are developed and applied to simulate material behaviors of CNT-reinforced concrete (Wang *et al.* 2017). Employed methods mainly involve continuum approaches such as meshless method (Wang and Liew 2015) and finite element method (Eftekhari *et al.* 2014). Discussions about fire safety issue are rare, while such discussions should be an essential prerequisite for actual applications of CNT-reinforced concrete. In this paper, aside from general introductions of the CNT-reinforcing technique, discussions on possible fire behaviors are also made.

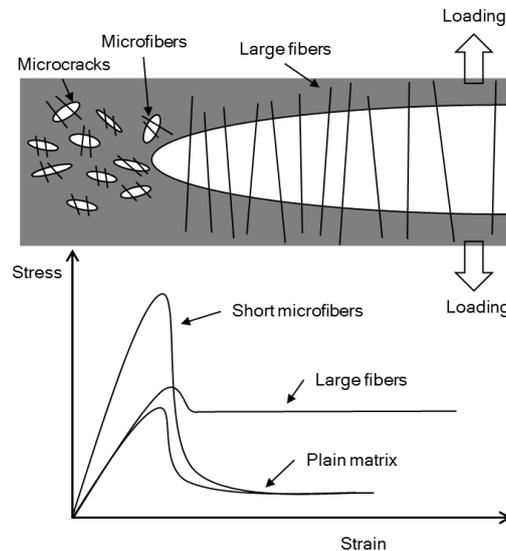


Fig. 1 Schematic diagram showing the general mechanism of fiber reinforcement in cement composite. Gray color indicates solid and white indicates void

This paper summarizes the current experimental works on CNT-reinforced concrete. The content covers FRC mechanism, CNT dispersion, CNT-cement structures, mechanical properties, fire safety and microstructures. The CNT reinforcing is regarded as a nanoscale FRC technique and CNTs are compared with other fibers such as steel and organic polymers. The fabrication method, CNT dispersion and the mechanical properties are introduced on the basis of existing experimental works. Schematic diagrams are included to demonstrate the principles of CNT dispersion, functionalization and mechanisms of the material enhancement. In reference to existing studies on bilayer composite material system, it is noticed that interface between dissimilar components is key to mechanical properties. The interface between CNT and cement matrix plays a critical role in determining the effectiveness of mechanical reinforcement. The fire safety issue and the microstructures are discussed with existing literature as well as our own evaluations. The interplay between CNTs and C-S-H is discussed with the illustrations by atomistic modeling.

2. Role of additional fibers in concrete

2.1 General reinforcing mechanism

Structural void is a critical concern about strength of solid materials such as epoxy, concrete and bonded composites (Hansen 1965, Landis *et al.* 2016, Tam and Lau 2015, 2016). Adding fibers to bridge voids or cracks is an effective way to mechanical enhancement (Brandt 2008, Metaxa and Shah). In order to improve the mechanical properties of cement, the selected fibers to add should feature with high aspect ratio, high elastic modulus and tensile strength. Steel is a commonly used material. Steel rebar and steel fiber are large-scale reinforcing components. Besides, relatively small-scale fibers are also used, they are mainly organic polymers such as polypropylene, polyethylene, polyolefin, polyvinyl alcohol (PVA) (Brandt 2008). The dimensions

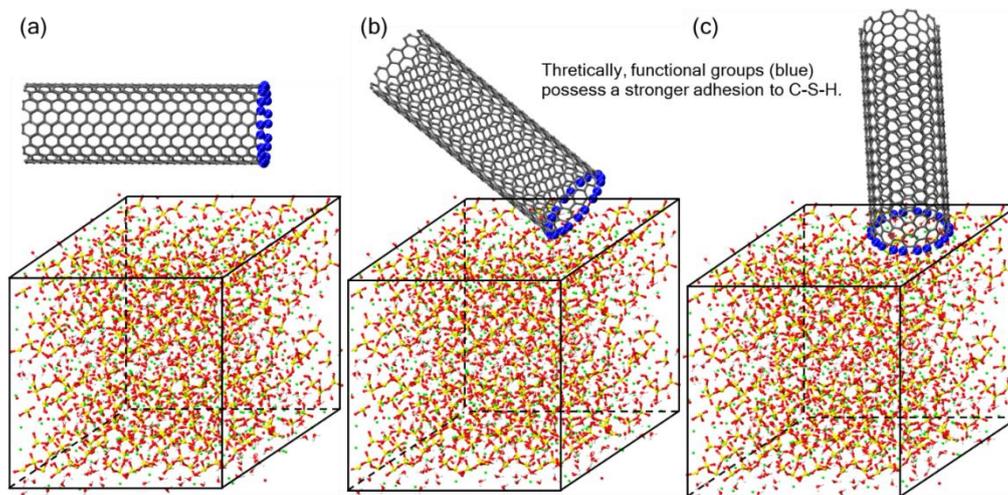


Fig. 2 Schematic drawings of interaction between functionalized CNTs and cement hydrates (C-S-H). Black frame outlines C-S-H gel, where calcium, silicon, hydrogen and oxygen atoms are in green, yellow, white and red respectively. CNT is in gray and representative functional groups are in blue. (a) A single-walled CNT aligns parallel to C-S-H surface. (b) Due to strong adhesion between functional groups (in blue) and C-S-H, the CNT inclines. (c) The CNT chooses a favorable adhesion site

of those reinforcing fibers range from micrometer to centimeter. The added fibers could act as binding and stress-transfer phases in cement and schematic drawings reproduced after (Betterman *et al.* 1995) in Fig. 1 can briefly introduce the mechanism.

Because concrete contains various dissimilar components, cracks are unavoidable defects lowering the fracture strength. Fig. 1 shows that in fracture process zone the fibers can impede propagation of crack tip so as to increase the energy required to break the material. As a result, fracture resistance of concrete can be improved. At the nanoscale, it is expected that CNTs can act as a similar binding phase which connects separate C-S-H particles and provides cohesive strength. The reinforcing effect of CNTs is critically determined by the interface adhesion between CNTs and C-S-H.

2.2 Interface between dissimilar components in composite

In composite material, the interface between dissimilar components is a critical part which determines the material properties of the composite (Scrivener *et al.* 2004). The materials interface can be quantified by its strength defined as bond quality or adhesion strength (Lau and Büyüköztürk 2010, Lau *et al.* 2012). The bond quality can be measured by multi-scale experiments (Lau *et al.* 2014, Qiu and Lau 2016) and predicted by molecular dynamics simulations (Büyüköztürk *et al.* 2011, Yu and Lau 2015a, Yu *et al.* 2014). Mechanical strength of interface critically determines fracture behavior and material strength of the entire composite (Yu and Lau 2015b). It has been revealed that the bilayer materials interface is typically the weakest part in a composite system and is susceptible to external conditioning. For example, in FRP-reinforced beams, moisture-influenced adhesion between FRP and base material determines flexural strength (Tam *et al.* 2016) and ductility (Gunes *et al.* 2013) of such bilayer material system. In steel bar reinforcement, corrosion that degrades bond quality is also a necessary concern (Holland *et al.*

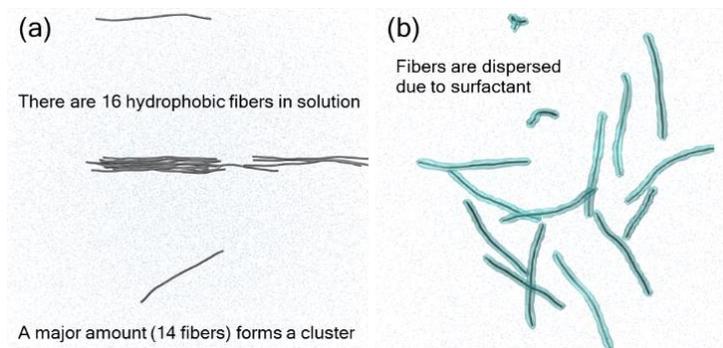


Fig. 3 Schematic drawings of (a) CNTs agglomerates and (b) dispersed CNTs by surfactants. CNTs are represented by chains in gray, water is represented by small dots in light blue and wrapping surfactants are represented by cyan bubbles

2016, Prieto Rabade *et al.* 2013). Such concept, i.e., interface plays a critical role, would also be adopted when studying FRC technique. In material system of FRC, the fiber-cement interface strength is essentially related to the pulling-out behavior, which determines how tightly the fiber is anchored to cement matrix and how effective the reinforcement is. Nanostructures of the fiber-cement interface (Shalchy and Rahbar 2015) has been found to be important for adhesion strength. Highly polarized functional groups such as carboxyl in organic fibers are strong adhesion sites for C-S-H. At the CNT-cement interface, the highly hydrophobic nature of CNTs might make water-rich region unfavorable for the nanotubes to adhere to. Also, low surface charge of CNTs leads to relatively weak adhesion with C-S-H. Not adequate adhesion between CNTs and cement matrix may lead to sliding, which disables the stress-transfer capability. Introducing functional groups to CNTs is an effective approach to enhance the adhesion between CNTs and hydration products (calcium hydroxide and C-S-H) in cement (Li *et al.* 2005). The functionalization can be achieved by multiple approaches via covalent (introduce functional groups such as -COOH) as well as non-covalent methods (polymer wrapping and surfactant adsorption) (Geng *et al.* 2008, Hirsch 2002, Ma *et al.* 2010). Schematic drawings can reflect the enhanced adhesion between functionalized CNTs and cement hydrates. On the basis of above theories, a thought experiment is demonstrated in Fig. 2. Initially we align a horizontal CNT over a plain C-S-H surface. This CNT has two kinds of terminus, which include an unmodified terminal at left and a functionalized terminal at right (with functional groups represented by blue beads) as shown in Fig. 2(a). As aforementioned, the functionalized terminal has a stronger adhesion to C-S-H than the plain carbon terminal does. Therefore, the initially horizontal CNT would incline to right and attach to C-S-H, as shown in Fig. 2(b). Eventually the attachment would be achieved and the CNT becomes vertical as shown in Fig. 2(c). This theoretical interaction between CNT and C-S-H indicates that functionalization is a method to improve the effectiveness of CNT-reinforcing to cement matrix.

3. Experimental works on CNT-reinforced cement

3.1 Fabrication methods

In the fabrication of CNT-reinforced cement, the most critical part is the dispersion of CNTs.

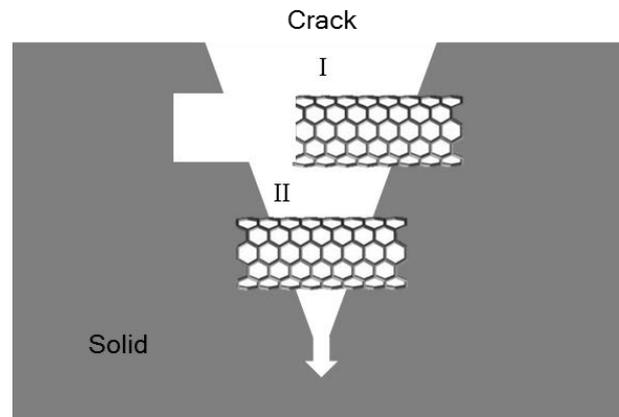


Fig. 4 Schematic diagram of CNTs connecting C-S-H particles, reproduced from (Nadiv *et al.* 2016). Type I represents fracture pulling out, type II represents bridging effect

CNTs can be dispersed into water solution and then mixed with cement mortar. However, due to large surface-to-volume ratio, strong van der Waals interaction and highly hydrophobic nature, CNTs often form agglomerates instead of individual filaments in aqueous solution. Straightforward approach to distribute the CNTs agglomerates solution to cement mortar does not make an adequate dispersion, which lead to ineffective mechanical reinforcement. To disperse CNT clusters as individual filaments, surfactants addition and ultrasonication are useful treatments. The ultrasonication can break CNTs agglomerates into individual filaments and ideally the surfactant could wrap around at the surface of each CNT (Richard *et al.* 2003, Yurekli *et al.* 2004), as shown in Fig. 3. Molecular structure of surfactant is featured with one hydrophobic end which is favorable to be attached to CNTs, together with another hydrophilic end which is soluble into water. An individual CNT filament surrounded by surfactant molecules can be well dispersed into solution by ultrasonication and can be then used to prepare hydrated cement pastes. The addition of surfactants could therefore improve the dispersion of CNTs into cement and concrete. Effective surfactants include sodium dodecyl sulfate (SDS), acetone, sulfuric acid and nitric acid. (Collins *et al.* 2012, Hunashyal *et al.* 2011, Konsta-Gdoutos *et al.* 2010a, Luo *et al.* 2009, Metaxa *et al.* 2013, Musso *et al.* 2009, Yu *et al.* 2007, Metaxa and Shah). In most studies, the type of CNTs belong to multi-walled CNTs, whose diameter is 2-30 nanometer and length is up to 50 micrometers (Han *et al.* 2015). A summary of the fabrication methods can be found in a table in (Parveen *et al.* 2013). Some water reducer, or superplasticizer (Abu Al-Rub *et al.* 2012), can also constitute as surfactant. Pre-fabricated well-dispersed admixture of CNTs is also a useful dispersing method (Metaxa *et al.* 2012). With considerations based on interatomic interactions between carbon materials and C-S-H, chemical modifications of CNTs and addition of graphene oxide are also adopted for dispersion to improve the adhesion between CNTs and C-S-H (Lu *et al.* 2015). Meanwhile, direct growth of CNTs and carbon nanofibers (CNF) on cement has also been reported (Hlavacek *et al.* 2011, Ludvig *et al.* 2011, Mudimela *et al.* 2009, Nasibulin *et al.* 2013, Sun *et al.* 2013).

3.2 Characterizations of CNT-reinforced cement

Two material properties are important indicators of the quality of a CNT-reinforced

cementitious material system, including the dispersion of CNTs and the mechanical enhancement. To characterize the dispersion of CNTs in cement, methods applied include atomic-force microscopy (AFM), scanning electronic microscope (SEM) and transmission electron microscopy (TEM). To characterize the mechanical enhancement brought by CNTs-reinforcement, methods applied are generic mechanical testing programs such as compressive test, tensile test and four-point bending test. In addition, measurements of the porosity, pore size distribution and microscopic mechanical properties by porosimetry have also been reported (Konsta-Gdoutos *et al.* 2010b, Nochaiya and Chaipanich 2011). With CNTs-reinforcement, the concrete shows reduced porosity. Many studies have reported enhanced material properties of CNT-reinforced concrete. A summary of the mechanical enhancement can be found (Han *et al.* 2015). It is noticed that the concentration of CNTs ranges from 0.1% to 2% in weight. When CNTs are added, concrete could benefit from an increase of compressive strength by more than 20%. Besides, mechanical properties such as tensile strength, hardness, stiffness, flexural strength, fracture toughness, ductility are also enhanced. The ratio of enhancement is typically more than 20%. Reinforcing mechanism of CNTs is similar to FRC concept, as shown in Fig. 4.

3.3 Discussions on fire safety

Construction materials have a close relationship with daily life, where safety is the first priority. Evaluation of material behavior under extreme conditions such as fire exposure is necessary for safety protection (Chow *et al.* 2006). Fire safety is a comprehensive consideration from multiple aspects and can be evaluated by theoretical inferences, experiments as well as numerical calculations (Chow and Chow 2010, Chow and Chow 2009, Lau *et al.* 2016). With mechanical enhancement, intuitively one would expect a better fire resistance of concrete structures. However, material properties are dynamic at elevated temperature condition. When concrete is exposed to fire, degradation of mechanical properties is almost unavoidable due to numerous physical and chemical changes (Fletcher *et al.* 2006). First of all, liquid water in concrete will vaporize at the temperature over 100°C. This leads to significant increase in pore pressure inside concrete. Next, when the temperature goes up to 400°C, calcium hydroxide starts to decompose, bringing a significant reduction in material strength. At higher temperature, aggregates will deform or decompose, causing severe structural defects. Generally concrete will be significantly degraded at a critical temperature of around 600°C, where different thermal responses between aggregates and cement matrix could lead to cracking and spalling. Spalling is a major concern that initiates cracks and fractures of concrete in fire. High-strength concretes are even more susceptible to the risk of spalling due to their high compactness, dense microstructure and low permeability compared to normal concrete. Hence, a research question comes up, discussing about whether CNT-reinforced concrete is more sensitive to fire or not. Experimental studies on high-temperature behavior of CNT-reinforced concrete are limited, while we can refer to studies on fiber-reinforced (Banggi and Horiguchi 2011, Khaliq and Kodur 2011, Ngo *et al.* 2014), nanomaterial-reinforced high-performance concretes (Heikal *et al.* 2015, Kodur and Phan 2007, Lo Monte *et al.* 2015) as well as the spalling mechanisms (Fletcher *et al.* 2006, Yu *et al.* 2016). Spalling is resulted from prevailing of excessive pore pressure over tensile strength and is induced by fast heating as well as intense vaporization. One way to retard spalling is to dissipate the pore pressure before it exceeds the tensile strength of the microstructure. In fiber-reinforced concrete (FRC), organic polymers such as polypropylene (Kalifa *et al.* 2001) would melt by high temperature and form channels inside cement to retard the fire-induced intense vaporization of internal water. CNTs are too small to

form the vapor channels. Another approach is to improve the tensile strength of the pore structure so that the pore pressure cannot easily break the structure. Adding CNTs could enhance the tensile strength of concrete at nanoscale and provides resistance against spalling.

Other concerns about fire include flammability and toxicity. Studies have reported retarded flammability of CNT-reinforced composite materials (Kashiwagi *et al.* 2005, Kashiwagi *et al.* 2004). It has been reported that CNTs can form a shield-like layer to slow the thermal degradation of polymer nanocomposite. As a result, the introduction of CNTs should at least not increase the risk of burning for concrete. In terms of toxicity, because CNTs are made of carbon, the full combustion products (carbon dioxide) are not toxic, while the product from incomplete combustion (carbon monoxide) might be harmful. Nonetheless, CNTs themselves could be harmful to human body because of the small size. During material fabrication, service life or fire exposure, CNTs might escape from concrete to air and be absorbed into respiratory system. Considering the typical concentration of CNTs for reinforcement (about 1% in weight) and the mass of concrete buildings, we expect that the air might be significantly polluted by released CNTs, which might cause damage to organs of respiration. This potentially detrimental effect could be prevented by proper fabrication of CNT-reinforced concrete which completely encapsulates the nanoparticles inside the concrete.

4. Atomistic models of C-S-H and CNTs

4.1 C-S-H nanobranched

Calcium silicate hydrate (C-S-H) is a mesoporous gel-like material. Current description of C-S-H involves a colloidal model, which contains granular C-S-H particles with a characteristic length of around 4 nm (Allen *et al.* 2007). Internal structure of the C-S-H particle is layer-like (Chiang *et al.* 2012) and is composed of alternative layers of solid silica/calcium and water molecules. As the understandings of C-S-H reach to nanoscale, molecular dynamics simulations become a useful investigation tool for structural and mechanical properties. Due to elusive nanostructure of amorphous C-S-H, exact atomistic modeling is hard to achieve. Atomistic models of C-S-H could be developed out of crystalline structures of tobermorite by randomly removing certain amount of silica tetrahedron and inserting water molecules. A previous study (Pellenq *et al.* 2009) has reported a realistic C-S-H model, which has achieved reasonably good agreement with experiments in terms of mechanical properties, density and X-ray powder diffraction (XRD) intensities. Many following studies have constructed relatively large-scale C-S-H models through atomistic (Hou *et al.* 2014, Yu and Lau 2015c) as well as coarse-grained modeling (Lau *et al.* 2015, Masoero *et al.* 2012, Yu *et al.* 2016) and investigated the material properties. Among them, a nano-branched C-S-H structure (Dolado *et al.* 2011) that reconciles well with existing colloidal models could be a reasonable starting point to construct CNT-reinforced C-S-H models. Because CNTs are added to cement before hydration, they can act as cores for hydration products to precipitate. It is expected that the formed C-S-H would wrap around CNT. In other words, void space in C-S-H would be filled with CNT. The nano-branched C-S-H structure contains a nanoscale pore with a diameter of around 4 nm, which is a potential site for CNTs to stay. The model can represent local structures of the CNT-embedded C-S-H.

4.2 Incorporation of a single-walled CNT into C-S-H branch

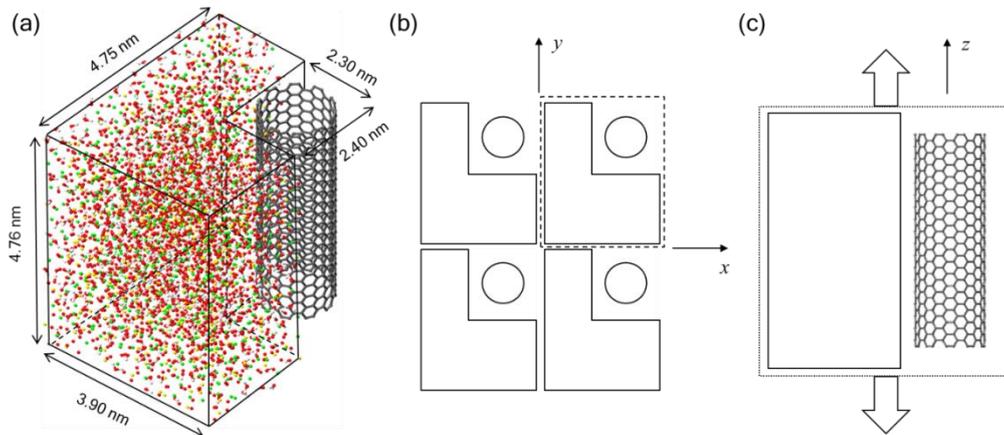


Fig. 5 (a) Snapshots of a single-walled CNT-embedded L-shaped C-S-H. (b) Periodic boundary condition scheme showing repeating images at x and y axis. Tensile tests are performed. (c) Tensile test performed along the longitudinal direction (z axis)

Table 1 Tensile modulus of C-S-H nanobranched model and CNT-embedded model at 300 K and 600 K

Direction	Tensile modulus (GPa) at 300 K		Tensile modulus (GPa) at 600 K	
	CSH nanobranched	CNT embedded	CSH nanobranched	CNT embedded
x	23.04	22.38	19.74	17.06
y	20.66	19.64	15.28	11.76
z	23.91	81.86	18.06	72.99

Following the concept of C-S-H nanobranched, we construct a similar L-shaped atomistic model. This C-S-H model is reproduced from (Pellenq *et al.* 2009) by replication and clip. The dimensions of the model are shown in Fig. 5(a). A (10, 10) single-walled CNT with 4.3-nm length is inserted at the corner. A momentum fix is employed to control movement and rotation of the CNT in order to simulate a CNT that is long enough to penetrate the C-S-H nanobranched. Periodic boundary condition is applied in all three directions, as shown in Fig. 5(b) for demonstration in x and y axis. Non-bonded interactions between carbon atoms and C-S-H are derived from CSHFF force field (Shahsavari *et al.* 2011) is used to govern the interaction of C-S-H. LAMMPS (Plimpton 1995) is employed to run molecular dynamics simulations. Equilibrium is performed using a NPT ensemble with temperature controlled at 300 K or 600 K and pressure controlled at 1 atm. After 1-ns running, root-mean-square deviation (RMSD) reaches a plateau, indicating that equilibrium has been achieved and the systems are ready for tensile tests.

4.3 Mechanical properties of CNT-embedded C-S-H

Tensile tests of C-S-H are performed in 3 axial directions with and without CNT at normal temperature (300 K) and elevated temperature (600 K). As mentioned before, temperature affecting CNT/cement system can be as low as 500 K. Above 500 K, the morphology of the CNT/cement matrix surface becomes ill-crystallized. The simulation with 600 K temperature can capture morphology change and demonstrate the effect of morphology change. From 700 K to 900

K, the decomposition of cement hydrates begins. Because empirical molecular dynamics simulations cannot reproduce C-S-H decomposition at this temperature range, material behaviors of CNT and cement at higher temperatures reported by an experimental study can be referred to (Zhang *et al.* 2017). The tensile test is based on strain-control scheme and the strain rate is about 1 nanometer per nanosecond. The corresponding strain rate is around $2 \times 10^{-6} \text{ ps}^{-1}$, which permits a rational tensile testing for both CNT and C-S-H (Hou *et al.* 2014, Wei *et al.* 2003). Results are listed in Table 1. The typical tensile modulus of the C-S-H nanobranche is around 20 GPa, lower than other molecular dynamics results (around 50 GPa). This discrepancy arises from the partially occupied cross-section area of the model, i.e., C-S-H does not fill the entire load-bearing cross section in full. The effective loading area to cross-section area ratio is approximately 2.35/4.70. A simple transition can make current modulus values comparable to results in literature, e.g., at 300 K, tensile modulus of C-S-H nanobranche along x axis is 23.04 GPa with ratio of occupancy to be 2.35/4.70 so the reproduced tensile strength is 46 GPa, comparable to literature. Significant tensile modulus improvement is found along the longitudinal directions (z axis) of the embedded CNT. This is due to superior axial tensile strength of CNT, as shown in Fig. 5(c). Meanwhile, it is noticed that the side-direction (x and y) tensile modulus of CNT-embedded model drops by around 10%. At 600 K case, y -direction modulus even drops from 15.28 GPa to 11.76 GPa. This is probably caused by swelling of CNT. The embedded CNT is slightly compressed in transverse directions (along x and y) before tensile test. At the initial stage of tensile test, CNT tends to swell a bit and the swelling leads to reduction in tensile stress. Comparing the tensile modulus at different temperatures, a drop of around 20% is observable. This phenomenon indicates reduced mechanical properties of C-S-H at elevated-temperature conditions (below 600 K), where CNT can still provide extraneous reinforcement. However, as temperature goes up to 700 K, 900 K and higher values, reinforcement from CNT would lose due to decomposition of cement hydrates (Zhang *et al.* 2017). This result implies that CNT can protect cement from structural deformation, while cannot prevent chemical decomposition.

5. Summarized evaluations of CNT reinforcement

In this paper, CNT reinforcement is regarded as an effective nanoscale FRC technique in compensate to micro- and macro-scale fiber reinforcements. CNT reinforcing technique is evaluated with attention to CNT-cement interface, CNT dispersion, mechanical enhancement, fire behavior. In summary, CNT reinforcement is effective for mechanical performance of concrete and may not bring detrimental side effect to fire resistant capability of concrete. However, due the small size and incompatibility with cement, CNTs might escape from concrete during fire and enter human body, causing potential damage. This kind of damage could be prevented by properly fabricated CNT-reinforced concretes with a complete encapsulation of the harmful nanoparticles. Also, an atomistic model of CNT-embedded C-S-H is constructed on the basis of nanobranche structure. The porous nature of C-S-H nanobranche permits the incorporation of a single-walled CNT. Molecular dynamics simulations are performed to measure tensile modulus of C-S-H nanobranche with CNT embedment at room temperature and elevated temperature. It is found that introduction of CNT is thermally stable and can significantly enhance tensile strength along the longitudinal directions of CNT but could induce a slight drop in tensile modulus at other directions.

6. Future challenges

Nanomaterials can bring significant changes to macroscopic performance of materials. However, such variation is often diverse due to different fabrication methods and nanomaterial properties. CNT mechanical reinforcement has been proven to be effective for concrete, with a variety of fabrication methods and testing programs. Based on continuous studies, repeatable, large-scale, relatively low-cost and environmentally friendly fabrication methods should be gradually established. Meanwhile, characterization techniques for *in situ* detection of CNTs dispersion within concrete requires further development. To obtain more information about the fire safety issue, future works may involve experiments about thermal responses of CNT-reinforced concrete at elevated temperatures as well.

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