

Nano to Microlevel Modeling of Cement-Based Materials

by E.A.B. Koenders, J.S. Dolado, K. van Breugel, and A. Porro

Synopsis: Recent developments in nanotechnology paved the way for deepening the modeling level of science-based kernels and enabling new opportunities in terms of understanding the formation of hydration products and their contribution to the microstructure. Based on these developments next generation models are considered to have the potential to design new advanced materials that contribute to sustainable construction. One of the activities currently running in this field is the Codice (COMputationally Driven design of Innovative CEment-based materials) project which is a multi-scale modeling research project established within the European research arena FP7. The project has the ambition to bridge the nanoscale to the microscale by applying advanced computational simulation modeling techniques for cementitious materials. Nano-based models will be connected to the microscale level within the framework of the Hymostruc model. It is the objective of the CODICE project to provide more insight into the role of the fundamental building blocks of CSH gel (basically 5nm sized nanoparticles) and the mechanisms that govern their aggregation into high-density (HD) and low-density (LD) C-S-H varieties. Thus, the project aims to refine the microstructure of the Hymostruc model (Breugel 1991) so as to recognize the two types of C-S-H aggregates. The new computational scheme is expected to be a perfect tool to design new cementitious materials with improved mechanical properties.

Keywords: CSH gel; microstructure; modeling; nanotechnology.

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Eddy A.B. Koenders, PhD, is Associate Professor in the Department of Civil Engineering at Delft University of Technology. He received his MSc in offshore technology and his PhD in concrete structures from Delft University in The Netherlands. His research interests include hydration modeling, sustainable construction, and monitoring.

Jorge S. Dolado, PhD, is employed at Labein Tecnalia in Derio, Spain. He received his MSC and PhD from Valencia University and Basque University, respectively. His research interests include computational modeling at the nano level and CSH gel formation.

ACI Member **Klaas van Breugel**, PhD, is a Full Professor and Head of the Materials and Environment section of Delft University of Technology. He received both his MSc and PhD from Delft University of Technology in The Netherlands. His research interest include modeling, microstructure, structural safety, and visco-elastic behavior.

Antonio Porro, PhD, is Head of the Nanotechnology Department Nanoc of Labein Tecnalia, Derio, Spain. He received his MSc and PhD from Bilbao University and Basque University, respectively. His research interest include nanotechnology as a technological asset for the construction sector.

INTRODUCTION

Almost from the early start of the application concrete, the process of early hydration required the attention of many researchers. Already at the end of the eighteenth century, it was Tetmayer (1883) who was engaged with temperature measurements of early-age concrete. At the beginning of the nineteenth century, temperature effects in massive concrete structures were considered as a serious problem (Clover 1973). Onsite experimental programs were developed in order to control the concrete quality and to avoid unexpected harming of the concrete structure. Sometimes these experiments were supported by hand made temperature calculations and, based on this, early-age stresses and strength predictions were conducted. Substantial concessions had to be made regarding the interpretation of the mix design, properties, schematization and modeling approach. These concessions were related to the lack of knowledge about what was really going on inside the concrete and the fact that only very limited calculation tools and capacity were available that time. Those early days of modeling the hydrational behavior of cementitious materials are now definitely left behind. The pace of developments in the field of computational methods of hydration of cementitious materials has been tremendously. Nowadays, research results become available superfluously at a high rate and the availability of substantial computer power has become a common thing. Complex models used to analyze in-depth processes can be simulated at in an increasing level of detail. At this moment most computational models for cement hydration modeling have schematized the microstructure at the microlevel offering a clear picture of the processes that govern the hydration process of cementitious material. Albeit the final of modeling detail has not been reached yet, it still becomes clearer that the nano level is the level that has to be reached in order to be able to manipulate the original properties of a material. Many initiatives have been set in this field recently and others are already running to explore this particular field of science. A joined effort in this field is the EU CODICE project (CODICE 2008) titled “Computationally Driven design of Innovative Cement-based materials” and is developed within a consortium framework. The main objectives of the CODICE project are to develop serial parameter-passing multi-scale modeling schemes to monitor and predict:

- The (nano/micro)-structural formation and evolution of cementitious matrices as a function of macroscopic processing variables, such as the size of the cement grains, water/cement ratio, cement grain composition, etc.
- The degradation (aging) of cementitious structures subjected to osteoporosis-like chemical degradation processes, as a function of macroscopic processing variables.
- The mechanical performance of cementitious skeletons given their (nano/micro)-structure (accurate structure-performance linkage).

Without these joint efforts, it is considered to be impossible to make concrete a ‘predictable material’. The question arising from these numerical challenges will be discussed in this paper. First the basic concept of cement hydration is discussed followed by an historical overview addressing the developments of hydration models ending up with a list of the currently most used models in this field. Next the challenges in the field of nanotechnology will be discussed in view of the activities that run under the CODICE umbrella. Finally, the paper ends up with a retrospective view about computational modeling in view of the future ambitions and conclusions.

THE HARDENING PROCESS—THE BASIC CONCEPT

Cement can be considered as a granular material. The dimensions of the particles vary from $1\text{ }\mu\text{m}$ (0.000039 in.) up to about $100\text{ }\mu\text{m}$ (0.0029 in.). The particles are irregular shaped and exhibit a complex chemical composition. The most important phases identified within cement are the calcium silicates (C_3S and C_2S), calcium aluminate (C_3A) and calcium aluminate ferrite (C_4AF). When coming into contact with water, chemical reactions will commence while contributing to the formation of a solid microstructure. At first a short reaction will take place where a small percentage of the available C_3A will dissolve and reacts with the gypsum forming tricalcium sulfate. In addition, ettringite is being formed that possesses a needle shaped structure. These needles form a spatial framework in between the hydrating cement particles (Fig. 1, stage a and b). With ongoing hydration, the spatial framework will be occupied gradually by means of the development of calcium silicates hydrates (C-S-H gel). These silicate hydrates are formed close to the surface of cement particles. At the same time, crystal shaped calcium hydroxides are formed that likely precipitate in water rich spaces. During the process of hydration, reaction products are being formed with the property that the volume of the reaction products is smaller than the volume of the original reactants. This volume reduction is generally known as chemical shrinkage and is contributing to densify the reaction products. As the thickness of the shell of hydration products surrounding a hydrating cement particle is increasing, it is becoming more and more difficult for ions to diffuse through this shell and to pass the distance towards the anhydrous cement grain, or the other way around. The cement reaction becomes diffusion controlled and is retarding the overall rate of reaction of the hydration process (Fig. 1, stage c and d).

TOWARDS HYDRATION MODELS

Over the years, researchers have proposed models that were able to simulate the progress of the hydration process and could be used as a basis to estimate the associated properties. In this respect, the single particle model of Pommersheim (1980) can be considered as one of the most advanced approaches for simulating the hydration of tricalcium silicate hydrate. In these days, Pommersheim distinguished different kinds of hydration products viz. the ‘inner product’, the ‘middle layer’ and the ‘outer product’ (see Fig. 2). The middle layer is considered to be a layer which goes into solution and which is hard to penetrate. The inner and outer products are considered to have different densities with a different diffusivity resistance. With the use of basic numerical techniques, the rate of degeneration of the middle layer and the diffusion coefficients of the inner and outer products could be tuned in such a way that an accurate ‘fit’ for the experimentally determined hydration curves could be reached. However, this model didn’t address the effect of the particle size distribution.

With the simulation model HYMOSTRUC (Breugel 1991), Van Breugel developed a full particle-based microstructural simulation model that accounts explicitly for the particle size distribution, the chemical composition, the water-cement ratio and the hydration temperature. The model follows a statistical basis for the inter-particle distances and calculates the formation of microstructure according to a so-called particle embedding mechanism. The model can be used to calculate a virtual microstructure and enables the possibility to calculate the associating material properties. Figure 3 shows an example of a simulated virtual microstructure (water/cement = 0.3) at three different stages of the degree of hydration, i.e. $\alpha_h = 0\%$, 20% , and 50% . In the simulations are carried out for cement, particles are ‘stacked in space’ at random locations. The cubic sample includes particles with diameters ranging between 1 and $37\text{ }\mu\text{m}$ (0.000039 and 0.00145 in.).

Still the most advanced operational hydration model is the model developed by Bentz and Garboczi (1991) at NIST. In the beginning of the nineties they introduced the pixel-based model called CEMHYD3D. A cementitious microstructure is considered to be built up from elements, called pixels, representing a volume of $1\text{ }\mu\text{m}^3$ ($1.31 \times 10^{-12}\text{ yd}^3$). Initially, cement grains are stacked at random in a 3-D space or a digitized scan of a microstructure is used as the simulations’ initial state. At the borders of the cement grains, pixels go into solution and optionally react with other pixels under the formation reaction products. CEMHYD3D is a fundamental model and suitable to examine the hydration process at the microlevel. At this moment, new initiatives are being exploited at NIST and focus on the hydration model that has its roots at the nano scale level, called HydratiCA (Bullard 2009). This model incorporates schemes for the basic chemical and physical processes for simulating the hydration process (Fig. 4).

NANOSCALE SIMULATION

With the European CODICE project it is the ambition to introduce nanotechnology in simulation models for cement hydration and to make these advanced technologies applicable for the construction sector. Within the framework of a model, nanotechnology-based models for C-S-H gel formation will be implemented and connected

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to the microlevel model Hymostruc by using a multiscale modeling approach. Research activities take place at the nano-, sub-nano, and the microlevel. Emphasis is on modeling C-S-H gel formation and the (re)use of this information at the microlevel to increase the modeling accuracy and to be able to predict more advanced materials properties as well. The basic structure of the CODICE project is provided in Fig. 5. The tasks of CODICE exhibit a clear interconnectivity, showing clear feedback at a threefold level:

- Firstly at the level of the formation, hydration and evolution of cementitious skeletons, in which there is a clear feedback between the multi-scale modeling of the formation and evolution of cementitious skeletons and the experimental validation of the formation of cementitious skeletons.
- Secondly at the mechanical performance of the cementitious skeletons, in which there is an analogous feedback between multi-scale modeling of the “bearing capacity” of the cementitious structures and its experimental validation of the performance of the computationally-driven designs.
- Finally, the project has a third loop connecting formation, hydration and evolution and mechanical performance, accounting for the fact that wise designs must be guided by structure-performance linkages.

With regard to the CODICE project it is stressed that different iterations are planned to feedback the microstructures’ mechanical performance. The starting criterion that links the microstructure to its performance will be the most appealing designs that correspond to those with lower (micro)-porosities and higher volume fractions of the C-S-H gel.

DOWNSCALING MICROSTRUCTURE

When considering the geometrical gap between the micro and the nano level it has to be noticed that 3 orders of magnitude have to be downscaled. The microstructural-based models like those being implemented in Hymostruc or the NIST model CEMHYD3D have common working dimensions of $100 \times 100 \times 100 \mu\text{m}^3$ ($0.0039 \times 0.0039 \times 0.0039 \text{ in.}$) (see Fig. 5) representing a microstructure built up from anhydrous cement particles, hydration product (inner and outer) and a capillary pore structure. By bridging the gap with the nanolevel the microlevel sample has to be downsized and the interface with the nano level has to address the physical and chemical processes that are active on the much smaller scale level (see Fig. 6). In this respect, nano-based numerical models simulate the formation of C-S-H gel and the formation of hydration products at the atomistic level. When upscaling this information and considering the microlevel models as the level to connect to, it can be observed that the formation of hydration products at the microlevel model becomes visible in terms of the inner and outer hydration products. With the simulation of the formation of hydration products at the nanolevel and upscaling this information towards the microlevel, a much more detailed view on the morphological formation of chemical bindings can be taken into account. In Fig. 6 this are the shells that surround the anhydrous grains and mimics the formation of hydration products. The products that grow in outward direction account for the formation of structure, i.e. represented by the relative amount of chemical bindings. Besides, the formation of hydration products at the nanolevel, it also provides the opportunity to pave the way for the development of cementitious materials possessing new or improved properties and complying with the requirements of the client to a larger extent. It is a way toward the development of a multi-scale computational model for the design of tailor made cementitious materials.

NANOLEVEL CHALLENGES

Albeit the C-S-H gel constitutes the main ingredient of cementitious skeletons and their life-service depends crucially on it, the possibility of tuning the intrinsic nature and properties of the C-S-H gel has been simply out of reach. Fortunately this long-standing impossibility can be currently overcome by the complementary action of new experimental capacities and stronger simulations schemes which explicitly pay attention to the nanoscale. Recent nanoindentation experiments (Acker 2001; Constantinidis 2004) have revealed that the C-S-H gel can present itself either in a low stiffness and low density variety (called LD C-S-H gel) or in a variety with a high stiffness and high density (called HD C-S-H gel). This dissimilar bearing capacity is indeed much more pronounced in their resistance to osteoporosis-like degradation processes. The question that arises is straightforward: Could the formation of the stronger and more durable HD C-S-H varieties be promoted over the LD- ones?

It must be admitted that at present, our knowledge on C-S-H gel is too vague so as to realistically face such a challenge. Our incomplete picture of C-S-H gel basically relies on two complementary visions, each one oriented to explain different sizes and phenomena (see Fig. 7). On the one hand, several works have centered their analysis on the recognition of the structural features of C-S-H gel at the molecular level. It is well recognized that C-S-H gel exhibits a short-ordering alike to that of distorted tobermorite and jennite crystals (Taylor 1984; Richardson

1992; Cong 1998) (Fig. 7(a)). On the other hand, other strain of research has paid attention to the recognition of the colloidal properties of C-S-H gel (Powers 1960; Sereda 1970; Wittmann 1979). Current model is the Jennings's model (Jennings 2000). This model basically considers that the C-S-H gel is composed of approximately 5 nm (0.0000002 in.) sized rounded particles, which, in turn, aggregate to form high-density (HD) C-S-H or low-density (LD) C-S-H depending on a packing factor (Fig. 7(b)).

Unfortunately it is still unclear nowadays how to link the short-ranged structures with the colloidal particles. It is clear, therefore, that an ineludible prerequisite prior to any realistic technological possibility is to obtain further knowledge on the short-range ordering of C-S-H particles the colloidal models start from; namely we need to change our current picture of these basic C-S-H bricks (based on ~5 nm [0.0000002 in.] sized particles) by an improved version which accurately accounts for their real morphology and chemistry.

In this scenario, any hint on the structure of C-S-H gels that can be given by modeling and numerical simulations would be tremendously beneficial. Although atomistic simulations have been barely applied to deal with C-S-H gel, there is lately a great agreement that they represent an unmatched opportunity to unravel the smallest features of C-S-H gel. Some progress has been made so far. For instance, it is worth noting that recent Molecular Dynamic (MD) simulations have reproduced many important features of the cementitious C-S-H gels (the mean chain length, number of Ca-OH and Si-OH bonds, etc.) that, up to now, were only inferred from experiments (Dolado 2007). These calculations must be taken as an appropriate starting point for more accurate descriptions which could predict the sizes and shapes of the smallest C-S-H features as a function of the composition. Lets note that though Small Angle Neutron Scattering (SANS) experiments (Allen 2007) seem to be consistent with the 5 nm (0.0000002 in.) sized particles Jennings's model refers to, other techniques support other sizes and morphologies. From Atomic Force Microscope (AFM) measurements Nonat (2004) and Plassard (2004) suggest that the basic C-S-H bricks are 60 x 30 x 5 nm (0.0000024 x 0.0000012 x 0.0000002 in.) particles, whereas based on Transmission Electron Microscopy (TEM), Richardson (2004) recognizes 3 to 8 nm (0.00000012 to 0.00000032 in.) globular particles within the so-called Inner product (Ip) and thin particles of and variable length and about 3 nm (0.00000012 in.) in their smallest dimension within the Outer product (Op). Our feeling is that MD simulations are on the verge of identifying the basic C-S-H bricks and bridging the existing gap between the structural and colloidal visions of C-S-H gel.

Once the basic building blocks (BBB) of C-S-H gel are identified through MD simulations, the link with the aforementioned hydration models could be feasible by invoking the granular nature of C-S-H gel (Constantinidis 2007). After defining a "resolution" length L (~ 500 nm [0.00002 in.]), which is accessible to the microscale models, a sub-microscale piece of C-S-H gel (of generic $C_{na}S_{nb}H_c$ stoichiometry) can be refined by taking advantage that it basically consists of aggregations or repetitions of n BBBs (of generic $C_aS_bH_\Omega$ stoichiometry and size a_{BBB}), as schematically depicted in Fig. 8. Hence, different computational techniques can be (a priori) easily implemented so as to refine the structures derived from the hydration models. Differently to above mentioned MD simulations, which explicitly accounts for the atomic composition of the basic building bricks, the foreseen computational schemes might directly work with the basic particles. The simplest approach might be the use of Packing Algorithms (PA), which are very efficient computationally speaking but neglect the physical and chemical aspects of packing. Alternatively one might resort to Monte Carlo simulations where chemical reactions could intervene by defining appropriate inter-particle potentials. One possibility is to this end is the employment of the insights gained from MD simulations to define C-S-H particles decorated on their surfaces by appropriate Si-OH and Ca-OH bonds. The main drawback of both the PA and the MC simulations is that they provide useful information about the equilibrium configuration but say nothing about the kinetical and dynamical aspects of the aggregation process. Much more physical but much less computationally efficient methods like Distinct Element Methods (DEM) or Brownian Cluster Dynamics (BCD) could be used whenever the dynamical aspects are required.

Finally, it should be remarked that the above described nano-refinement of the microstructure can also be employed to determine the elastic properties of the cementitious skeletons. One possibility rests on solving the continuum linear elastic equations over Representative Elementary Volumes (REV) by means of standard Finite Element Model (FEM) or Finite Volume Model (FVE) simulations, in which the elasticity matrix $\{D_{el}\}$ at the nodes are provided by sub-micro and nano-scale simulations (see Fig. 9). After dividing a REV of side L_{REV} into voxels, the hydration models can be employed to say the actual chemical (or crystalline) composition of the voxel (C_3S , C_2S , Aft, C-S-H, etc.). With this knowledge, the elastic matrix at a point X ($\{D_{el}\}_X$) can be calculated through nano-simulations which give the intrinsic Young modulus E and Poisson ratio ν of the voxel. Lets note that recent atomistic simulations have been already able to predict both the intrinsic elastic properties of the most important

crystalline phases present in cement paste and even the experimental range observed for the stiffness of C-S-H gel once the intrinsic nanoporosity and the finite chain length of the silicate chains are properly accounted for (Manzano 2009).

CONCLUSIONS

With the CODICE project, it is the ambition to answer computational challenges that are required when bridging the gap between nano- and micro-scale modeling of cementitious materials by means of advanced computational simulations. In fact CODICE project aims to develop a serial parameter-passing multi-scale modeling scheme to predict the structural evolution and the mechanical performance of non-degraded and degraded cementitious matrices as a function of macroscopic processing variables to guide the design of cementitious materials in which the HD-C-S-H forms are promoted over the LD- C-S-H ones.

CODICE's computational toolkits expected to boost the competitiveness of the European Construction sector, since it will provide valuable and affordable tools to:

- Optimize the processes of cement production and to minimize its environmental impact.
- Decrease significantly the time and the costs of the quality control assessments.
- Enable the possibility to design new advanced sustainable materials.
- Provide flexibility in the use of performance design mixtures for the construction sector.
- Optimize the design of cementitious materials (either in terms of their mechanical performance or their life-cycle analysis).

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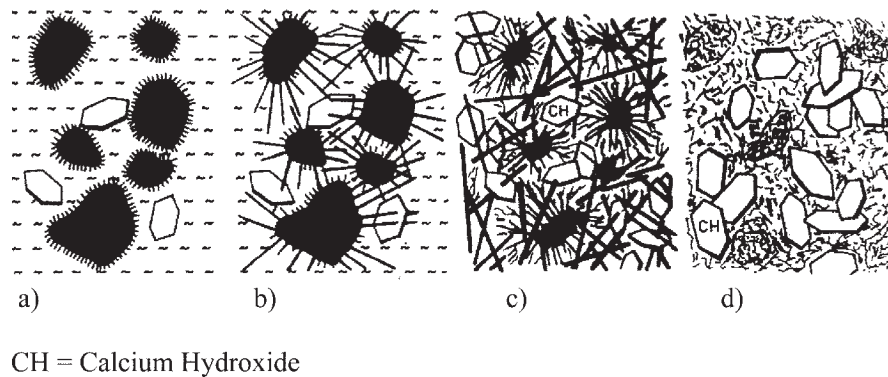


Fig. 1—Development of structure in cement-based materials (schematic, after Locher 1976): (a) plastic phase; (b) "setting" phase; (c) basis skeleton; and (d) stable skeleton.

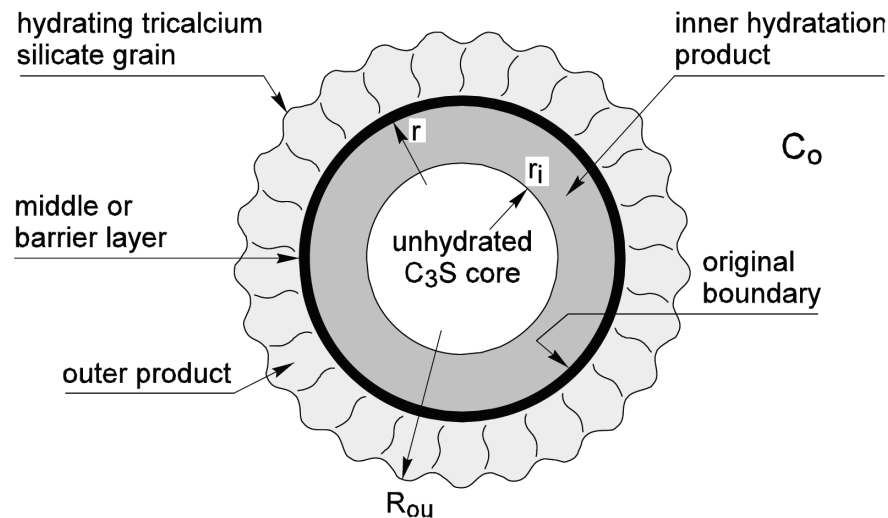


Fig. 2—Single particle model for hydration of tri-silicate according to Pommersheim (1980).

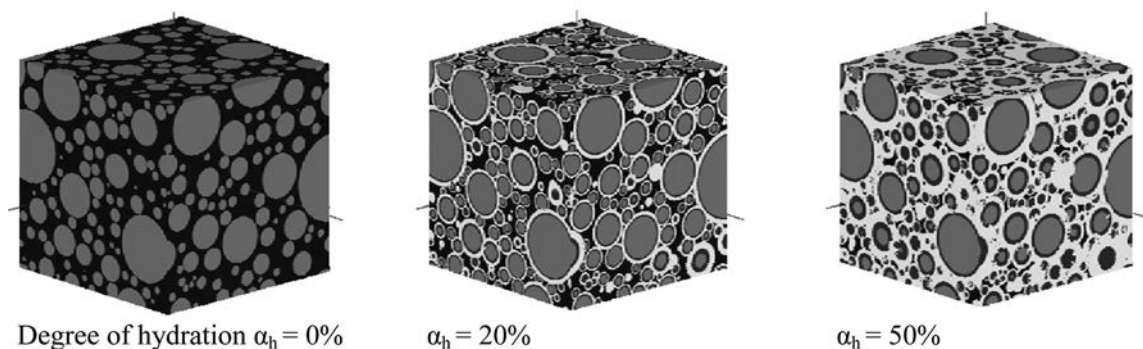


Fig. 3—Virtual microstructures of cement paste for three different stages of the hydration process, that is, $\alpha_h = 0$, 20, and 50%, simulated with Hymostruc (Breugel 1991). Water-cement ratio = 0.3.

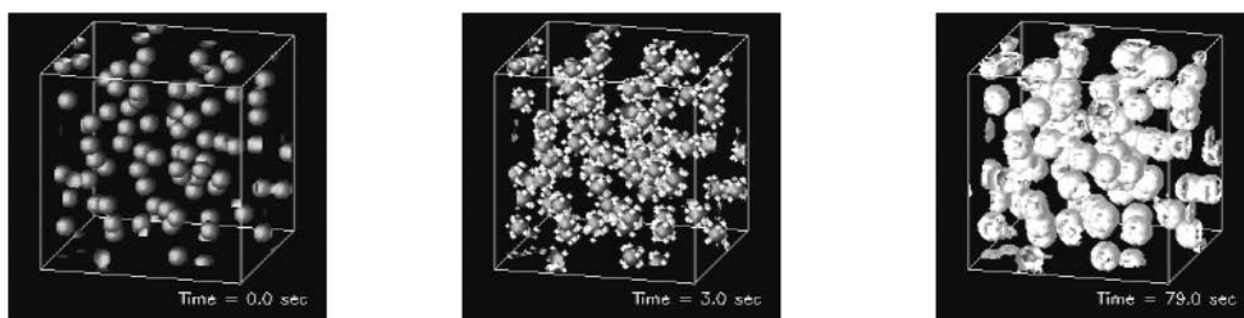


Fig. 4—Impression of a simulation conducted with the HydratiCA model (Bullard 2009).

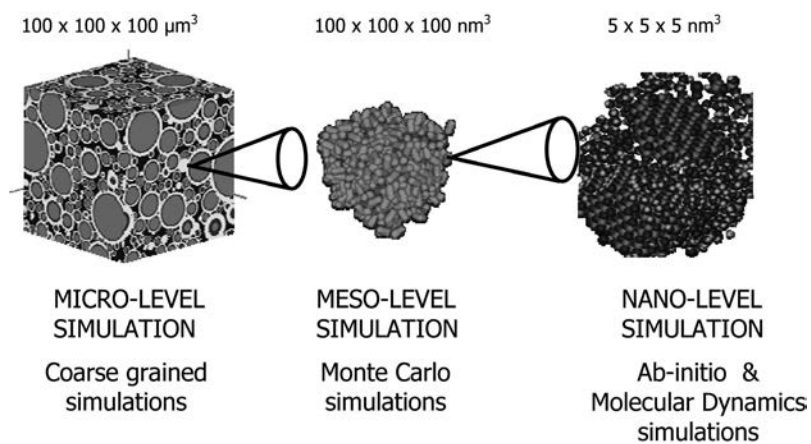


Fig. 5—Schematic impression of the multi-scale modeling approach conducted within the CODICE project.

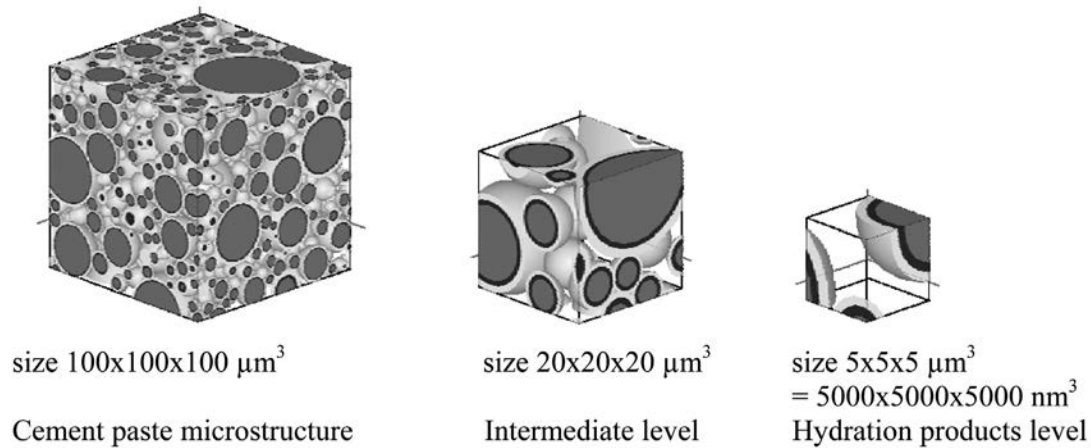


Fig. 6—Downsampling the virtual microstructure from the microlevel toward the nanolevel.

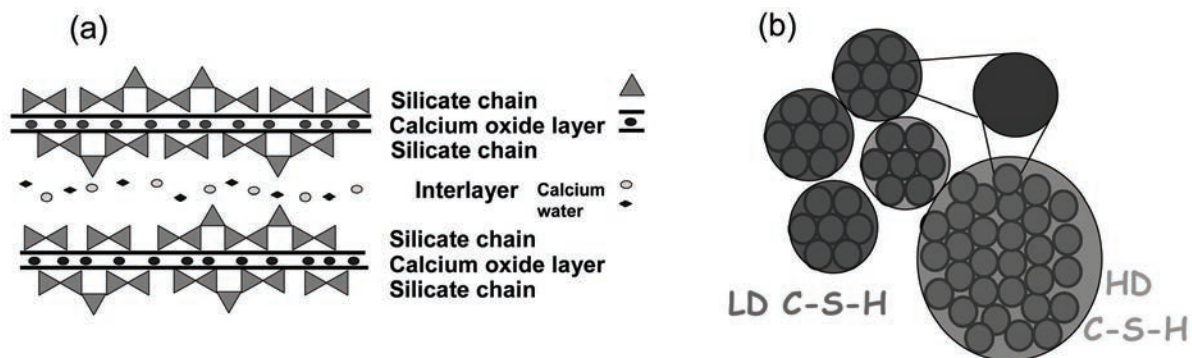


Fig. 7—Schematic representation of the two main visions for C-S-H gel: (a) structural model that describes the atomic scale of the C-S-H gel as an imperfect and disordered crystalline calcium silicate; and (b) colloidal model for the arrangement at the nanoscale of C-S-H gel nanoparticles.

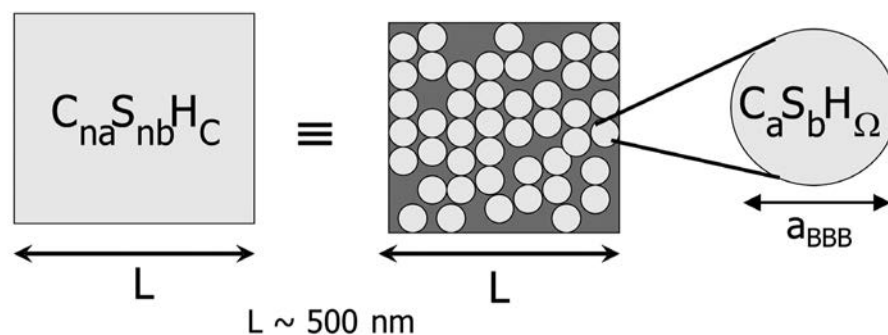


Fig. 8—Bridge from the microstructure and nanostructure. Note that as an appealing first approach, the Ca/Si of the BBBs can be taken as the same that the one appearing at the micro-level.

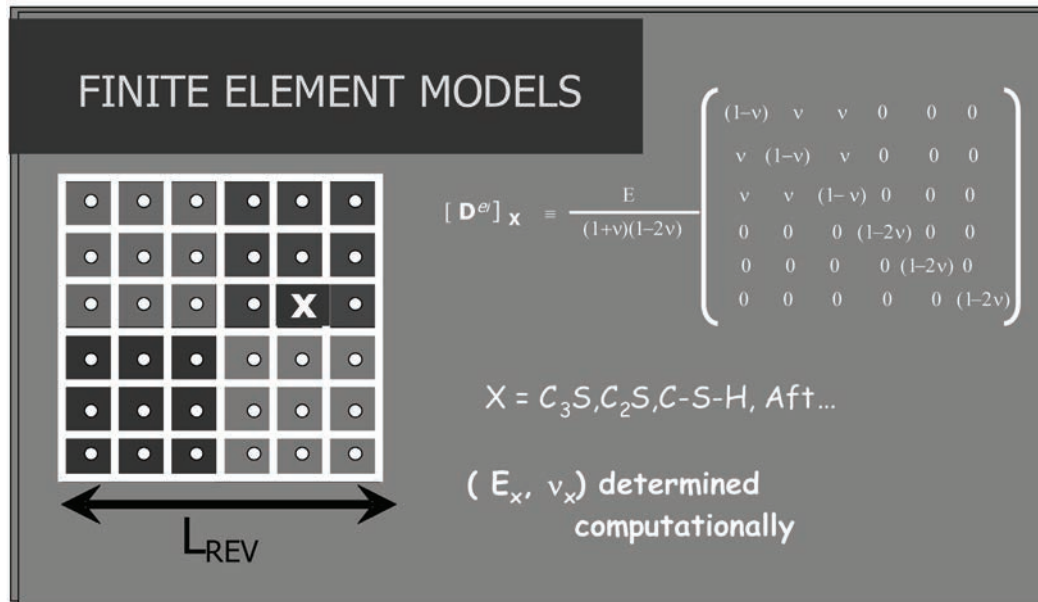


Fig. 9—One possibility to calculate the elastic properties of cementitious skeletons is based on finite element models, where the inputs at the nodes account for the nanostructure.

Carbon Nanotubes Reinforced Concrete

by Z.S. Metaxa, M.S. Konsta-Gdoutos, and S.P. Shah

Synopsis: In this study, the development of cementitious nanocomposites reinforced with multiwall carbon nanotubes (MWCNTs) at water-cement ratios of 0.3 and 0.5 was investigated. The effect of carbon nanotubes at low concentrations on the fracture properties, nanoscale properties and microstructure of the nanocomposite materials was studied. The morphology and the microstructure of nanocomposite samples were investigated using an ultra high resolution field emission scanning electron microscope. A special type of nanoindenter, along with in-place scanning probe microscopy imaging, was used to determine the local nanoscale mechanical properties. The results show that the mechanical properties of cementitious matrices can be increased by the incorporation of very low amounts of CNTs. Nanoimaging of the fracture surfaces of cement nanocomposites have shown that CNTs reinforce cement paste by bridging the nanocracks and pores. Additionally, nanoindentation results suggest that CNTs modify and reinforce the nanostructure of cement paste by increasing the amount of high stiffness C-S-H and reducing the porosity.

Keywords: carbon nanotubes; mechanical properties; nanofiber reinforcement; nanoindentation; scanning electron microscopy.

ACI member **Zoi S. Metaxa** is a PhD Candidate at Democritus University of Thrace, Greece, and a Visiting Predoctoral Fellow at the Center for Advanced Cement-Based Materials (ACBM) at Northwestern University, Evanston, IL. She received her BS and MS in civil engineering from Democritus University of Thrace in 2005 and 2007, respectively. Her research interests include concrete nanocomposites, concrete rheology, and fracture mechanics of concrete.

ACI member **Maria S. Konsta-Gdoutos** is an Associate Professor and Director of Section of Mechanics of the Department of Civil Engineering of Democritus University of Thrace. Her research interests include investigations into the relationships between microstructure and performance of advanced cement-based materials, high performance structural materials, concrete composites, and nanocomposites.

Surendra P. Shah, FACI, is the Walter P. Murphy Professor of Civil Engineering at Northwestern University and the Director of ACBM. His research interests include constitutive relationships, nondestructive testing, failure and fracture of concrete, durability, fiber-reinforced concrete, and self-consolidating concrete.

INTRODUCTION

Cementitious materials such as cement paste, mortar and concrete are principal materials for structures and they are widely used all over the world. Advanced technological aspects of cement based materials have recently focused on developing high-performance cement composites, which exhibit high compressive strengths. However, such high performance composites demonstrate brittle failure and low tensile capacity. These characteristics of cementitious materials are serious shortcomings that impose limitations on structural design and affect the long term durability of structures. Fibers are incorporated into cementitious matrices to overcome these weaknesses.¹ Reinforcement is typically provided using macrofibers and microfibers that reinforce at the millimeter and/or the microscale, respectively. However, cement matrices also exhibits defects at the nanoscale,² where traditional reinforcement is not effective.^{3,4}

One of the most advantageous nanomaterials for nano-reinforcement are carbon nanotubes (CNTs). CNTs are likely to have several advantages as reinforcement for cement based materials as compared to more traditional fibers. In particular, they exhibit significant greater strength and stiffness⁵⁻⁶ than conventional fibers, which should improve the overall mechanical behavior of the composite. They also have higher aspect ratios, and they are expected to effectively arrest the nanocracks and require significantly higher energy for crack propagation. Additionally, provided they are uniformly dispersed and mainly due to their nanoscale properties, CNTs are expected to be closely spaced in the cement matrix and reduce the fiber free area which leads to the strength increase of the composite.⁷ CNTs are expected to control the formation of nanocracks in the matrix, thus producing a high-performance cementitious nanocomposite.

The potential use of CNTs as reinforcement in cement based materials has been investigated by few researchers. The effect of 2.0 wt% CNTs in cement was investigated by Makar et al.⁸⁻⁹ using SEM and Vickers hardness measurements. The authors concluded that CNTs may affect the early hydration progress, producing higher hydration rates. In another study Li et al.¹⁰⁻¹¹ tried to improve the bonding between 0.5 wt% multiwall carbon nanotubes (MWCNTs) and cement matrix using a carboxylation procedure and obtained a 25% increase in flexural strength and a 19% increase in compressive strength. Saez de Ibarra et al.¹² investigated the reinforcing effect of both MWCNTs and single wall carbon nanotubes (SWCNTs) at the nanoscale properties of cement paste matrix using an atomic force microscopy (AFM) indentation technique and reported modest gains in the Young's modulus. Cwirzen et al.¹³⁻¹⁴ studied the mechanical properties of cement matrices reinforced with different concentrations of MWCNTs. They reported no increase in flexural strength. More recently, research by the authors of this paper has shown that addition of 0.048 wt% of cement MWCNTs improve the nano- and macromechanical properties of cement paste.¹⁵ In particular, a 50% increase of the Young's modulus of cement paste, with water to cement ratio of 0.5, was obtained by the addition of very low concentrations of CNTs.

In this study, the development of MWCNTs/cement high-performance nanocomposites with water to cement ratio of 0.3 and 0.5 ($w/c = 0.3$ and $w/c = 0.5$) was investigated. In addition the development of high-performance cement-based nanocomposites using a lower amount (0.025 wt%) of MWCNTs is presented and discussed. Effective dispersion of CNTs in water was achieved by applying ultrasonic energy and with the use of a commercially available surfactant, commonly used in cement based materials.¹⁵⁻¹⁶ Fracture mechanics tests as well as nanoindentation tests were performed to investigate the reinforcing effect of CNTs. Moreover, the morphology and the microstructure of nanocomposite samples were investigated using an ultra-high-resolution field emission scanning electron microscope.

RESEARCH SIGNIFICANCE

The development of new fibers at the nanoscale has opened a new field for research that focuses on nano-sized reinforcement within concrete. The incorporation of fibers at the nanoscale level is expected to control the nanocracks in the matrix and essentially create a new generation of a “crack-free cementitious material.” It is widely accepted that carbon nanotubes exhibit the most advantageous properties among different types of nanofibers. The goal of this research is to evaluate the effect of MWCNTs as a reinforcing material in concrete. This research provides a better understanding on the mechanical response of high-performance cementitious nanocomposites reinforced with low concentrations of well dispersed MWCNTs. It also provides insight into the nanostructure and the local mechanical properties of the nanocomposites. The MWCNTs are shown to enhance the mechanical performance and strongly reinforce the nanostructure of cement matrix.

EXPERIMENTAL STUDY

Preparation of the nanocomposites

In this study, two types of commercially available purified multiwall carbon nanotubes (MWCNTs) with the same diameter, but different lengths were used. The MWCNTs with an aspect ratio close to 700 were designated as short and those with an aspect ratio of 1600 were designated as long (Table 1). Both kinds of MWCNTs were produced by catalytic chemical vapor deposition (CCVD) of carbon. The cementitious material used was Type I ordinary portland cement (OPC). All materials were used as received.

To effectively disperse the MWCNTs in the mixing water, MWCNT suspensions were prepared. The MWCNTs were added in an aqueous surfactant solution and sonicated at room temperature following the method described in Reference 16. The sonicator was operated so as to deliver energy of 1900-2100 J/min (1401-1549 ft-lb/min). Based on the authors' previous research,¹⁶ a surfactant to MWCNTs weight ratio of 4.0 was used to ensure that the MWCNTs were homogeneously dispersed. After sonication, OPC was added to the MWCNT dispersions at a water-cement ratio (w/c) of 0.5 and 0.3. Mixes with MWCNT concentrations of 0.025 wt% and 0.048 wt% were prepared using long MWCNTs, while short MWCNTs were used to develop mixes with concentrations of 0.048 wt% and 0.08 wt%. The mixing of the materials was performed using a standard Hobart mixer according to the procedure outlined by ASTM C305. Following mixing, the material was cast in 20 x 20 x 80 mm (0.79 x 0.79 x 3.15 in.) molds. After demolding, the samples were cured in water saturated with lime until testing.

Scanning electron microscopy (SEM) was employed to initially evaluate the dispersion of the CNTs in the cementitious matrix. Fig. 1 shows typical SEM images of cement paste reinforced with CNTs used as received, and dispersed following the aforementioned method. As expected, in the samples were no dispersion technique was employed (Fig. 1 (a)), large agglomerates and bundles of CNTs were observed. However, when CNTs were dispersed in the mixing water (Fig. 1 (b)), only individual CNTs could be identified on the fracture surface.

Test methods

The fracture surfaces of the nanocomposites were examined using two types of ultra-high resolution field emission scanning electron microscopes (Hitachi S5500 and LEO Gemini 1525) operated at 3 to 5 kV. Secondary electron (SE) imaging was used to obtain clear images at medium to high magnifications (10,000× to 150,000×). Small specimens of 25.4×6.35×6.35 mm (0.79×0.79×3.15 in) were prepared for each mix. After 18 hours of curing, specimens were demolded and kept in acetone to stop hydration. Prior to their observation, the Denton Desk III system was used to coat the fracture surface of the specimens with a 20 nm (7.87×10^{-7} in) thick layer of gold-palladium (Au/Pd).

Fracture mechanics tests were conducted to evaluate the performance of the nanocomposites. Notched specimens were tested at the age of 3, 7 and 28 days, by three-point bending. Based on ASTM C348, an average value of three specimens was used for each curing age. A water-cooled diamond saw was used to insert a 6 mm (0.24 in) notch into the specimens before testing. A closed-loop MTS servo-hydraulic testing machine with a 89 kN (20,000 lb) capacity was used to perform the test. To ensure stable crack propagation, a clip gauge was used to measure the crack mouth opening displacement (CMOD) and provide feedback to the loading machine. The rate of CMOD was set at 0.012 mm/min (4.72×10^{-4} in/min) and 0.009 mm/min (3.54×10^{-4} in/min) for samples with water to cement ratio of 0.5 and 0.3, respectively. The load versus CMOD graphs were created from the test results. Young's modulus was then calculated from these graphs using the two-parameter fracture model by Jenq and Shah¹⁷.

A commercially available triboindenter was used to determine the nanomechanical properties of the CNT composites. The triboindenter is a special type of nanoindenter that combines nanoindentation with high-

resolution in-situ scanning probe microscopy (SPM) imaging that allows pre- and post-test observation of the samples surface. Nanoindentation and SPM imaging was performed using a Berkovich tip with a total included angle of 142.3 degrees. Each indentation consisted of multiple cycles of partial loading and unloading, to eliminate creep and size effects.¹⁸ The nanoindentation depth, as a function of the imposed load, was recorded during the test. The mechanical properties were determined using the Oliver and Pharr method, where the indentation modulus is calculated from the final unloading curve¹⁹. Prismatic specimens of 25.4 x 6.35 x 6.35 mm (0.79 x 0.79 x 3.15 in.) were prepared and cured in water saturated with lime for 28 days. Before testing, thin sections of approximately 5 mm were cut out of the specimens, using a water cooled diamond saw, and mounted using an adhesive (softening temperature 71°C [160°F]) on a metal sample holder for polishing. The surfaces of the samples were polished using silicon carbide papers and diamond lapping films in order to obtain a very smooth and flat surface. An extremely smooth surface is necessary for the reliable determination of the local mechanical properties.² An optical microscope was, used at every step, to check the effectiveness of the polishing. In the final step, the polished samples were ultrasonically cleaned in water for one minute using a bath sonicator to remove polishing debris. To further investigate the effectiveness of the polishing procedure and find representative areas of the samples an environmental scanning electron microscope (ESEM), in low vacuum mode, was used. Prior to nanoindentation, the area was imaged using the Berkovich tip of the triboindenter to provide surface information and to ensure that the location of the nanoindentation is sufficiently smooth. Due to the highly heterogeneous nature of cement based materials, a large array of nanoindentations needed to be carried out²⁰. Each test consisted of 144 indents performed in a 12 x 12 grid (10 μm [3.94×10^{-4} in.] between adjacent grid points) with depths varying from 50 to 300 nm (1.97×10^{-6} to 11.81×10^{-6} in.). This procedure was repeated in at least three different areas on each sample. Irregular nanoindentation curves may occur due to the presence of large voids or cracking in the material²⁰ and can not be included in the analysis. The nanoindentation curves were examined in order to determine the validity of each indentation.

RESULTS AND DISCUSSION

Morphology and microstructure

The effect of the addition of 0.08 wt% short and 0.048 wt% long MWCNTs on the nanostructure of cement nanocomposites with a water-cement ratio of 0.5 is shown in Fig. 2(a) and (b). The figure illustrates SEM images of the fracture surface of the samples at a scale of 500 nm. It can be observed that in both cases MWCNTs are well dispersed in cement paste and only individual MWCNTs can be identified on the fracture surface. MWCNTs appear to be wrapped by the hydration products, indicating that good bonding between the carbon nanotubes and cement matrix is achieved. A good illustration of CNTs clearly bridging nanocracks and pores is shown on Fig. 2(a).

Macromechanical properties

A comparison of the average Young's modulus of nanocomposites with $w/c = 0.5$, reinforced with long MWCNTs at concentrations of 0.048 wt% and 0.025 wt% is shown in Fig. 3. It is obvious that a concentration of well dispersed long MWCNTs, as low as 0.025 wt%, can very effectively increase the Young's modulus by 55%. This result is of a very high importance from the cost point of view, since the lower the concentration of CNTs in the mix, the lower the cost of the nanocomposite. Table 2 compares the Young's modulus of 28 days nanocomposites, reinforced with 0.048 wt% and 0.08 wt% short MWCNTs, for w/c ratios of 0.5 and 0.3. It is shown that, samples reinforced with a lower concentration of short MWCNTs exhibit less increase in the Young's modulus, for both water to cement ratios. The mixes which demonstrated the highest increase in the Young's modulus for short and long MWCNTs at w/c of 0.5 and 0.3 are illustrated in Fig. 4(a) and (b), respectively. When compared to the plain OPC paste all MWCNT cement nanocomposites clearly exhibit an improved mechanical performance. It is also noticed that, independently from the water to cement ratio, specimens reinforced with either short MWCNTs at an amount of 0.08 wt% or long MWCNTs at an amount of 0.025 wt% provide the same level of mechanical performance. In general, higher concentrations of short MWCNTs are needed to reduce the fiber free area of the material and arrest the nanocracks. The results show that the length and consequently the aspect ratio of MWCNTs plays an important role in the reinforcing effect of cementitious materials. To further investigate the reinforcing mechanism of the CNTs, nanoindentation tests were performed on cement paste samples reinforced with MWCNTs.

Nanomechanical properties

Figure 5 shows the probability plot of the 28-day Young's modulus of plain cement paste and cement paste reinforced with 0.08 wt% short CNTs for water to cement ratios of 0.5 and 0.3, respectively. Values of the Young's

modulus up to 50 GPa (7252 ksi) are presented and the probability plots are calculated based on those values. The probability plots are in good agreement with results from the literature^{2, 20-21}. Values of the Young's modulus less than 50 GPa (7252 ksi) represent four different phases of cement paste corresponding to the porous phase, low stiffness C-S-H, high stiffness C-S-H and calcium hydroxide phase, while values greater than 50 GPa (7252 ksi) are attributed to nanoindentation on unhydrated particles (clinker phases) presented in the material.^{2, 20-21} The different phases have been found to exhibit properties that considered as distinct material properties and are independent of the mix proportions. As expected, the peak of the probability plots of plain cement paste with $w/c = 0.5$ and 0.3 falls in the area of the low stiffness C-S-H, which is the dominant phase of cement nanostructure. On the other hand, the peaks of the probability plots of the nanocomposites for both water to cement ratios are in the area of 20 to 25 GPa (2900 to 3625 ksi), which corresponds to the high stiffness C-S-H, suggesting that the addition of MWCNTs results to a stronger material with increased amount of high stiffness C-S-H. Moreover, it is observed that the probability of Young's modulus below 10 GPa (1450 ksi) is significantly reduced for the samples with MWCNTs for both water to cement ratios. The nanoindentation results provide an indirect method of estimating the volume fraction of the capillary pores²⁰ indicating that the MWCNTs reduce the amount of fine pores by filling the area between the C-S-H gel.

Nanoindentation of the phases of Portland cement (C_3S and alite, C_2S and belite, C_3A , C_4AF) have shown that the Young's modulus of the clinker phases range between 125 and 145 GPa (18,130 to 21,030 ksi).²² In addition, in a previous study² using the same type of cement and testing procedure, values of the Young's modulus of cement unhydrated particles close to 110 GPa (16,000 ksi) have been reported. Figure 6 shows typical $60 \times 60 \mu\text{m}$ ($2.36 \cdot 10^{-3} \times 2.36 \cdot 10^{-3}$ in.) AFM images, captured using the nanoindenter tip, of the nanostructure of cement paste with $w/c = 0.5$ and $w/c = 0.3$ reinforced with 0.08 wt% short MWCNTs prior to nanoindentation. The values of Young's modulus calculated from the grid indentation are reported on the images in GPa at the respective indent locations. It is observed that the stiffness varies reaching values as high as 185 GPa (26,832 ksi) which are attributed to the presence of unhydrated particles. The high values obtained from the nanocomposites indentation can be possibly attributed to the presence of CNTs in the vicinity of the unhydrated particles. Please note that the nanoindentation tip is in the order of 100 nm (3.94×10^{-6} in) and indentation on individual MWCNTs can not be distinguished. These results suggest that MWCNTs appear to alter the nanostructure of the cement matrix resulting in a stiffer and stronger material.

CONCLUSIONS

The reinforcing effects of multiwall carbon nanotubes (MWCNTs) in cementitious matrices with low and high water-cement ratio ($w/c = 0.3$ and $w/c = 0.5$) were investigated using fracture mechanics and nanoindentation tests. It was found that the mechanical properties of cement matrices can be increased using small amounts (0.025 wt% to 0.08 wt% of cement) of well dispersed MWCNTs. Specifically, samples reinforced with either long MWCNTs at a concentration of 0.025 wt% or short MWCNTs at an amount of 0.08 wt% exhibit similar increase in the Young's modulus, up to 55% and 37%, for nanocomposites with $w/c = 0.5$ and 0.3 , respectively. The nanoindentation results indicate that, independent of the water to cement ratio used, MWCNTs can strongly modify and reinforce the nanostructure of the cementitious matrix. When compared to plain cement, the nanocomposites exhibit reduced nanoporosity and increased amount of high stiffness C-S-H. Nanoimaging of the fracture surfaces of cement nanocomposites have shown that small quantities of well dispersed MWCNTs can enable the control of the cracks at the nanoscale level, and effectively reinforce the cement paste matrix by bridging the nanocracks and nanopores.

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Table 1—Properties of multiwall carbon nanotubes (MWCNTs)

	Aspect ratio	Diameter, nm	Length, μm	Purity, %	Surface area, m^2/g
Short	700	20-40	10-30	>95	110
Long	1600	20-40	10-100	>97	250-300

Note: $1 \text{ m}^2/\text{g} = 4882 \text{ ft}^2/\text{lb}$.

Table 2—Young's modulus in GPa (ksi) of 28 days nanocomposites reinforced with short MWCNTs

MWCNTs concentration	w/c = 0.5	w/c = 0.3
0.048 wt%	11.3 (1639)	19.4 (2814)
0.08 wt%	13.0 (1885)	21.8 (3162)

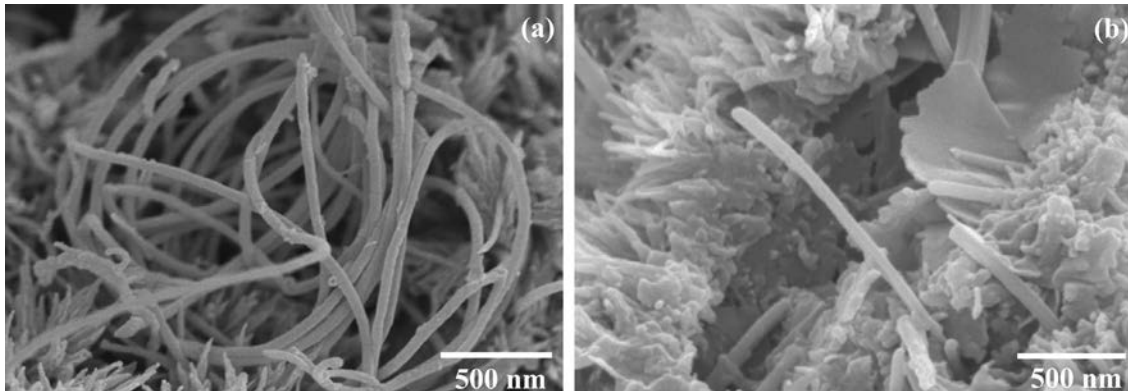


Fig. 1—SEM images of cement paste ($w/c = 0.5$) reinforced with: (a) as received MWCNTs; and (b) dispersed MWCNTs.

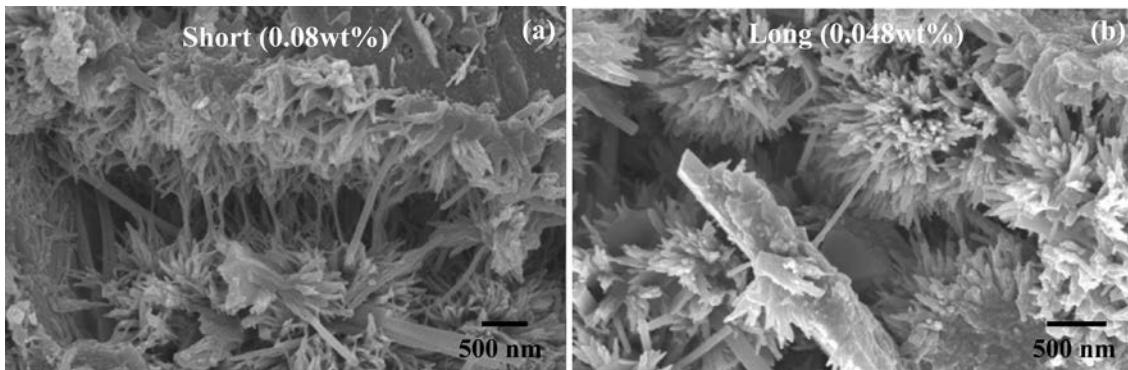


Fig. 2—Effect of: (a) 0.08 wt% short MWCNTs; and (b) 0.048 wt% long MWCNTs on the nanostructure of cementitious nanocomposites.

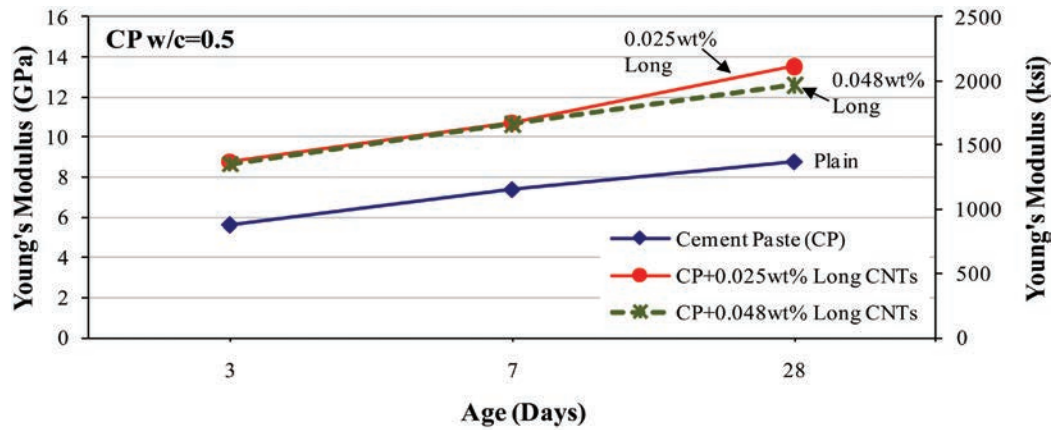


Fig. 3—Fracture mechanics test results of the Young's modulus of cement paste nanocomposites with $w/c = 0.5$ reinforced with 0.025 wt% and 0.048 wt% long MWCNTs.

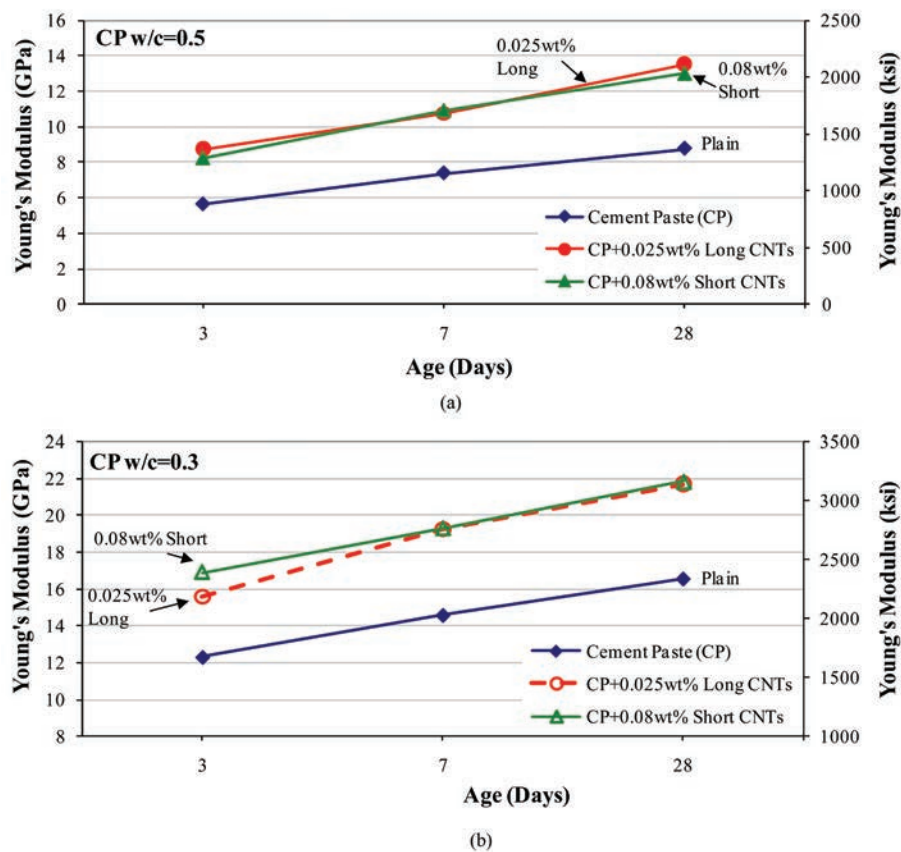
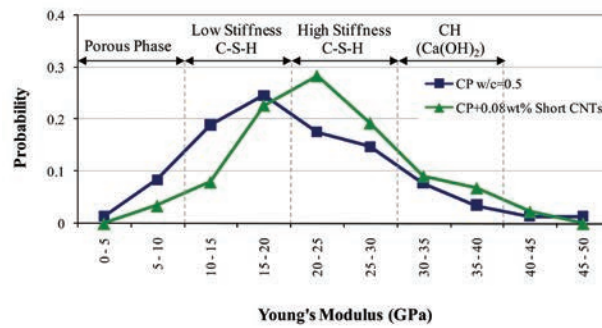
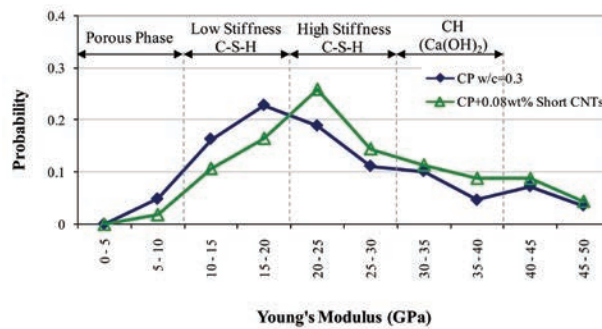


Fig. 4—Fracture mechanics test results of the Young's modulus of cement paste nanocomposites with: (a) $w/c = 0.5$; and (b) $w/c = 0.3$.

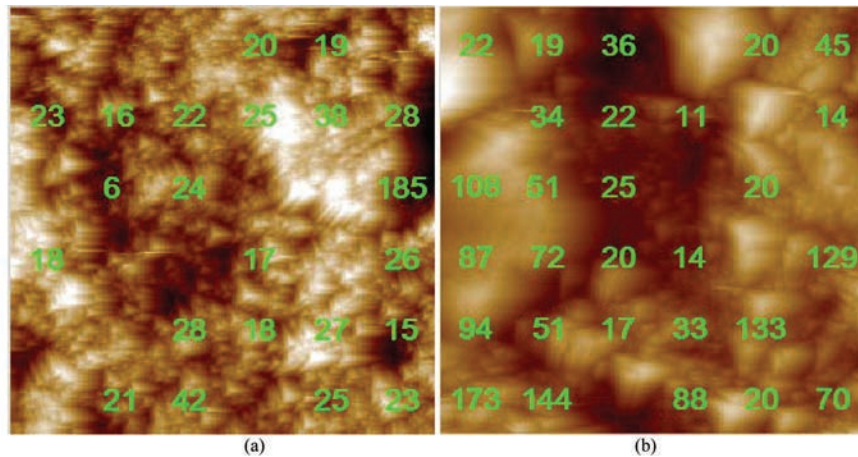


(a)



(b)

Fig. 5—Probability plots of the Young's modulus of 28 days cement paste and cement paste reinforced with 0.08 wt% short CNTs with: (a) $w/c = 0.5$; and (b) $w/c = 0.3$. (Note: 1 GPa = 145 ksi.)



(a)

(b)

Fig. 6—Typical $60 \times 60 \mu\text{m}$ AFM images of cement paste with: (a) $w/c = 0.5$; and (b) $w/c = 0.3$ reinforced with CNTs (0.08 wt% short) showing indentation modulus in GPa. (Note: 1 GPa = 145 ksi.)

Carbon Nano Filaments in Cementitious Materials: Some Issues on Dispersion and Interfacial Bond

by A. Yazdanbakhsh, Z.C. Grasley, B. Tyson, and R.K. Abu Al-Rub

Synopsis: Due to their excellent mechanical characteristics, carbon nanofibers (CNFs) and nanotubes (CNTs) are expected to enhance properties such as strength, ductility, and toughness in cementitious composites. However, such enhancements cannot be achieved unless the fibers are uniformly distributed in the composite and properly bonded to the matrix. CNT/Fs tend to agglomerate due to their high level of van der Waals interactions, and typically form a weak bond with hardened cement paste matrix. This work first presents a summary of the efforts made in the past to overcome these two problems. Some typical methods of qualifying/quantifying the dispersion of CNT/Fs either in the hardened cement paste or the mix water are discussed. To demonstrate the challenges associated with CNFs and their dispersion and interfacial bond with cementitious matrices, some of the results from an ongoing experimental program are presented. The experiments investigate the effect of surfactants on dispersion and their benefits and shortcomings when cementitious composites are concerned. It was shown that mixing cement and a well dispersed water-surfactant-CNF solution may not result in a uniform distribution of CNFs in the paste or an optimal CNT-matrix interfacial bond. However, it was also found that the interfacial bond can reach to a level high enough to prevent fiber pullout.

Keywords: carbon nanofiber; carbon nanotubes; dispersion; interfacial bond; surface modification; surfactants.

Ardavan Yazdanbakhsh is a PhD Student of civil engineering at Texas A&M University. He received his MS in civil engineering from the University of Sharjah, United Arab Emirates, in 2008. His research interests include the shear capacity of concrete elements, structural behavior of fiber reinforced concrete, reinforcement of cementitious materials with carbon nanofibers and nanotubes, and the design and development of stress-relaxing cementitious composites. He is an associate member of ACI Subcommittee 236-D, Nanotechnology of Concrete.

Zachary C. Grasley is an Assistant Professor in the materials division of the Zachry Department of Civil Engineering at Texas A&M University. He received his BS in civil engineering from Michigan Technological University and his MS and PhD in civil engineering from the University of Illinois, Urbana-Champaign. He is a member of ACI Committees 231, Properties of Concrete at Early Ages, and 236, Material Science of Concrete. His research interests include internal relative humidity, poromechanics, durability, viscoelasticity of concrete, and novel cementitious materials.

Bryan Tyson is currently seeking a Master of Science in civil engineering at Texas A&M University. He received his Bachelor of Science in civil engineering from Texas A&M University in 2008. His research interests include the reinforcement of cementitious materials with carbon nanofibers and nanotubes, finite element modeling, as well as analysis and design of intelligent structural systems using magnetorheological dampers.

Rashid K. Abu Al-Rub is an Assistant Professor of civil engineering at Texas A&M University. He received his BS and MS in civil engineering from Jordan University of Science and Technology, and his PhD in civil engineering from Louisiana State University. His research interests include computational solid mechanics, size-scale effects, nanocomposites, and constitutive modeling of the inelastic, damage, and fracture behavior of a wide range of engineering materials.

MOTIVATION AND OBJECTIVES

To develop approaches of harnessing the outstanding properties of CNT/Fs and use them as reinforcement in cementitious materials, it is important to know the methods developed to solve the two major issues of dispersion and interfacial bond. The first objective of this paper is to present a concise review of the research on dispersion and interfacial bond as reported in the literature. The second objective of this work is to demonstrate, through experimental results, the difficulties associated with incorporating CNFs in cementitious materials. Research on reinforcing cementitious materials with CNT/Fs is relatively new and the number of investigations and experiments focused on this subject, especially with CNFs, is still very limited. CNFs, although weaker than CNTs, still have very high tensile strength and modulus of elasticity. This paper reports on experimental investigations that study the dispersibility of CNFs and some issues related to their interfacial bond with cementitious matrices.

INTRODUCTION

In the past decade there has been growing interest in CNTs for various composite applications owing to their remarkable physical properties. Mechanically, they exhibit elastic moduli of more than 1 TPa (1.5×10^8 psi) (Salvetat and Kuik 1997). Their theoretical strength is 100 times that of steel, at only 1/6 the specific gravity (Wong et al. 1997). Values as high as 60 GPa (8.7×10^6 psi) for ultimate strength and 6% for ultimate strain have been reported (Walters et al. 1999; Yu et al. 2000). Salvetat and Kuik (1997) reported an elastic strain capacity of 12%, which is 60 times higher than that of steel. CNTs are also highly flexible, being capable of bending in circles or forming knots. Like macroscopic tubes, they can buckle or flatten under appropriate loadings (Lourie et al. 1998). Yakobson and Avouris (2001) summarize the mechanical behavior of CNTs. The mentioned values have been obtained mostly through theoretical calculations and estimations. Due to their extremely small size (their diameter is usually less than 20 nm) it is very difficult to measure the mechanical properties of CNTs directly. CNFs on the other hand are relatively large; their diameter can be as large as 200 nm. Recently, Ozkan et al. (2008) succeeded to perform direct measurements on CNFs. The CNFs that they investigated had a tensile strength between 2 to 5 GPa (2.9×10^5 to 7.3×10^5 psi) with an average modulus of elasticity of 300 GPa (4.4×10^7 psi).

Few studies have been carried out focusing on the effect of CNT/Fs on the mechanical properties of cementitious composites (Li et al. 2005; Trettin and Kowald 2005; Yakovlev et al. 2006; Yakovlev et al. 2006; Xiupeng Wang 2007; Cwirzen et al. 2008). These studies have shown that CNT/Fs can improve properties such as tensile and compressive strength. Although CNT/Fs are still too expensive to be used in large concrete structures such as buildings, bridges and pavements, the accelerating advances in the methods of producing these nano rein-

forcements are leading us to promising futures for CNT/F-reinforced cementitious composites (Nadarajah et al. 2008).

Two problems arise when using CNT/Fs to reinforce any kind of material. First, there is the question of dispersing them in the material; CNT/Fs attract each other with high magnitude due to van der Waal's forces. This results in the formation of agglomerations in the forms of entangled ropes and clumps which are very difficult to disentangle. Girifalco et al. (2000) showed that the cohesive energy between single-walled carbon nanotubes (SWCNTs) with a length of 100 nm to be about 2.9 keV. The dispersion problem has been combated using methods like surface modification of the fibers, surfactants in combination with sonication, and implanting or growing the fibers directly on non-hydrated cement grains.

The second problem limiting the effective use of CNT/Fs in cementitious materials is the difficulty in obtaining an optimal bond between the fibers and matrix due to the atomically smooth and nonreactive surface of these filaments (Lourie and Wagner 1998). Bonding is particularly an issue in cementitious composites as the interfacial bond between matrix and any type of straight fiber is relatively weak. If nanotubes are not completely dispersed and are assembled in bundles (ropes), there will be additional sliding inside the bundles (Ajayan et al. 2000). Surface modification is the most common way of enhancing interfacial bond. The surface of CNT/Fs can be functionalized to chemically react with cement hydration products, thereby creating stronger interfacial bond (Li et al. 2005). Most of the past experiments on CNT/F reinforced cementitious composites and the approaches chosen to address one or both of the mentioned problems are summarized in the next section. These experiments are almost exclusive to CNTs. Finally, an experimental program is presented which incorporates CNFs and the use of surfactants and ultrasonic processing to enhance their dispersion in water and cement paste.

DISPERSION, BOND, AND MECHANICAL PROPERTIES

Studies have shown that the wettability of CNTs in water is increased by the presence of polar impurities such as hydroxyl ($-OH$) or carboxyl ($-COOH$) end groups (Yao et al. 1998, Gogotsi et al. 2001, Gogotsi et al. 2002). Additionally, the studies of Ebbesen et al (1996) showed that the oxidation of CNTs cover their surface with carboxyl, carbonyl ($-C=O$), and hydroxyl groups, thereby improving their ability to disperse in aqueous solutions. Li et al. (2005) showed that these groups, as well as enhancing dispersion, react with calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) and lead to a strong covalent force on the interface between the fibers and matrix. One of the common methods of adding functionalized groups to the surface of CNTs is treating them with a solution of H_2SO_4 and HNO_3 (Eitan et al. 2003; Joonwon Bae 2002). In this method, CNTs are added to the acid solution and the oxidization is accelerated by using either reflux or sonication. In the sonication method, ultrasonic waves are transmitted from a probe into the liquid and produce alternate expansions and compressions. The pressure fluctuations give birth to microscopic bubbles (cavities), which expand during the negative pressure excursions and implode violently during the positive excursions. As the bubbles collapse, millions of shock waves, acoustic streaming, eddies and a combination of both pressure and temperature extremes are generated at the implosion sites. The cumulative amount of produced energy is extremely high and significantly accelerates chemical reactions and imposes dispersion (Timothy and John 2002).

The early experiments with acid treatment, perhaps due to procedure-related factors, did not show much improvement in mechanical properties of cementitious materials. Kowald (2004) used both acid treatment and sonication of CNTs in water and made cement paste specimen with CNT/cement weight ratios in the range of 0.5 to 5.0%. The CNTs had diameters between 10 and 30 nm and lengths between 1 and 10 μm . He tested the hardened specimens for compressive strength after 7, 14, and 28 days. Marginal improvements were observed in compressive strength and even a decrease in strength when the fiber dose was as high as 2.5% or more. Later, Li et al. (2005) performed a set of experiments with CNTs which had diameters and lengths at the ranges of 10-30 nm and 0.5-500 μm respectively. The CNT/cement weight ratio was 0.5% and the ratio of water/cement/sand was 0.45:1:1.5. They did not apply sonication, but added methylcellulose (0.4% by weight of cement) to enhance dispersion. The bending and compression tests showed that the addition of acid treated CNTs increased the compressive and flexural strength by 19% and 25% respectively. The investigators later used a similar method, combined with the sonication of CNTs in water prior to the mixing procedure, and produced cement paste with CNT/cement weight ratio of 0.5% (Li et al. 2007). The SEM images of fractured surfaces of hardened specimens showed that acid treatment enhanced both dispersion and bond. Untreated CNTs formed meshwork in the matrix while the treated CNTs were randomly distributed and covered by C-S-H.

The dispersion of CNT/Fs can also be enhanced by using surfactants. Dispersion of CNTs in liquid media is a well researched topic and many surfactants, combined with sonication, have shown to be effective (Moore et al. 2003). The surfactants add charges or hydrophilic ends to the surface of CNTs while their bundles are exfoliated

by sonication. Cwirzen et al. (2008) used CNTs (diameter 10 nm, length 2–4 μm) functionalized with carboxyl groups. They dispersed the CNTs in water by sonication while using polyacrylic acid polymers as surfactant. Using a mix containing only 0.045% of the CNTs, they observed a significant increase (as high as 50%) in compressive strength. Trettin and Kowald (2005) briefly reported an experiment in which they used different types of polycarboxylate-based superplasticizers as surfactants to produce cementitious CNT-reinforced composites. The results of compressive and bending tests showed that the superplasticizers with longer lateral chains resulted in higher strength, which indicated better dispersion of CNTs and better interfacial bond between the fibers and matrix.

Another method to enhance dispersion of CNTs in cementitious composites is to distribute and attach the nanotubes to the surface of cement particles before hydration. Makar and Beaudoin (2004) dispersed CNTs (Single walled, diameter 1.4 nm) in ethanol by sonication, and then added cement to the liquid to form a slurry which was further sonicated for hours. The slurry was then allowed to dry and ground to form a powder. The SEM images of the powder show that grains of cement powder have been well coated with CNT bundles. Maker et al. (2005) later made cement paste using CNT-coated cement produced with a similar method. Through SEM imaging of the fractured surface of dry paste, they found that the distribution of the CNTs in the hydrated samples is not the same as seen on the non-hydrated cement grains. CNT bundles were smaller in apparent diameter and more widely distributed in the hydrated matrix. The smallest bundles imaged had diameters less than 5 nm, suggesting that they were composed of only a few 1.4 nm diameter single walled CNTs. Nasibulin et al. (2009) have recently developed a method to grow CNT/Fs directly on the surface of cement particles. They showed that the fibers were homogeneously dispersed in the paste made with the produced cement and intermingled with the products during the hydration process. Using this cement resulted in more than 100% increase in the compressive strength of hardened paste.

METHODS OF MEASURING DISPERSION

The most common way of evaluating the distribution of CNT/Fs in a composite is scanning electron microscopy (SEM). SEM is the only method that shows the actual distribution of CNT/Fs in the hardened matrix, while the other common methods measure dispersion in the water used for producing cement paste. SEM is therefore utilized for the final validation of dispersion in the cementitious matrix. Images are normally taken from the fractured surface of a material in order to observe the CNT/Fs projecting out of the matrix. When the CNT/Fs are introduced to the paste by initially adding them to the mixing water, a uniform distribution of fibers in the matrix cannot be expected if they were not dispersed well in the water. Several methods are used to qualify or quantify dispersion in water. Three common methods, namely optical microscopy, Transmission Electron Microscopy (TEM) and UV-visible spectroscopy are briefly discussed here.

Although CNTs are too small to be seen by means of optical microscopy, if they are poorly dispersed, the agglomerations can be identified by this method. Since CNFs are larger than CNTs, the quality of their dispersion is easier to study by optical microscopy. Transmission electron microscopy (TEM) is used in order to observe the dispersion of CNT/Fs with much higher magnifications. In TEM, the image is formed from the interactions of electrons transmitted in the form of a beam through a very thin specimen (few hundreds of nanometers). Since the specimen should be solid, the dispersion is usually frozen rapidly and maintained at cryogenic temperatures, generally liquid nitrogen temperatures (-196°C [-321°F]), in the form of amorphous ice.

Another common method of measuring dispersion in a transparent medium is ultraviolet-visible spectroscopy (UV-Vis). This method is based on the simple fact that the better CNT/Fs are dispersed in a liquid, the darker the dispersion is and therefore absorbs more light. Figure 1 shows three specimens of CNFs mixed in water. In the first specimen Fig. 1(a), CNFs were simply added to water and mixed by a hand-stirrer. In less than a minute after mixing, most of the CNFs settled down while a small portion floated at the top. In other words, there was no dispersion and the bulk liquid was completely transparent. In the second specimen (Fig. 1(b)), the CNFs were added and hand-mixed with a solution of water and surfactant. The CNFs were slightly dispersed and the specimen absorbed some light. Finally, in the third picture (Fig. 1(c)), the mixture of water, surfactant, and CNFs was sonicated for 10 minutes. This resulted in a good dispersion and the specimen absorbed a lot of light and was thus very dark.

The schematic layout of a UV-vis spectroscopy device is presented in Fig. 2. In each step of measurement, the source sends radiation of a certain wavelength (in UV-visible range) through two specimens. One of the specimens is the dispersion of particles (CNT/Fs) in a liquid medium such as water or a water-surfactant solution, and the other specimen is only the liquid medium without any particle. Based on the strength of the radiation transmitted through the specimens and collected by the detectors, the portion of radiation absorbed by the particles

is determined. CNT/Fs, if dispersed well, absorb the radiation of a specific range of wavelength depending on several parameters such as their size, length and shape. It has been shown that the wavelength range absorbed by some CNTs is between 200 and 350 nm, with an absorption peak at approximately 250 nm (Jiang et al. 2003; Yu et al. 2007). UV-vis spectroscopy is quantitative, accurate and simple, and is a useful means for drawing comparisons between dispersions made from one type of CNT/F. However, UV-vis does not provide information about the bundle size and the distribution pattern of CNT/Fs, while optical microscopy, TEM, and SEM, despite being qualitative, are direct and visual measures of dispersion. The next section presents the findings of an experimentation program using these three methods.

EXPERIMENTAL

The experimental investigations reported here aimed at studying the dispersibility of CNFs in aqueous solutions and cement paste, as well as characterizing the interfacial bond between CNFs and cement paste matrix. Solutions of CNFs in water was produced by different approaches and imaged by optical microscopy, and in one case with TEM. Subsequently, cement paste was made by either adding a CNF-water dispersion to cement or simply adding water to a dry mix of cement and CNFs. The fractured surface of hardened paste was imaged by SEM and some correlations and dissociation was found between the distribution of fibers in CNF-water dispersions, and in the paste specimens made from mixing the dispersions with cement. The SEM images of pulled-out and fractured CNFs were used to draw conclusions about the quality of interfacial bond between CNFs and cementitious matrix.

Materials and preparation of specimens

Two types of CNFs were investigated. Table 1 presents some information about dimension and surface area of the fibers as well as the methods used to study their dispersion. The first type has an average diameter of 150 nm and length in the 10-20 μm range. The CNFs were provided by Showa Denko Group under the commercial name VGCF-H. The dispersion of the VGCF-H fibers in water was studied by optical microscopy, and their distribution in hardened cement paste was observed by SEM. The second type of CNF has a diameter between 60 to 150 nm and a length between 30 and 100 μm . The fibers were provided by Applied Science Company under the commercial name Pyrograph PR-24 (PS), referred to hereafter as Pyrograph. The Pyrograph fibers were studied using optical microscopy, SEM, and also TEM.

Most of the dispersions were made by ultrasonically processing the CNFs in a water-surfactant solution for 15 minutes. A Sonics & Materials (Vibra-Cell) model VC-505, 20 kHz liquid processor with a 1/2 in. (12.7 mm) diameter titanium alloy probe was used at an amplitude setting of 50%. Two types of surfactants were used in this study. The first was a nonionic surfactant provided by BASF with the commercial name Pluronic F98. Moore et al. compared this surfactant with several other surfactants and found it effective for dispersing CNTs in water (Moore et al. 2003). The second surfactant was a superplasticizer; a high range polycarboxylate-based water reducing admixture provided by W.R. Grace with the commercial name ADVA Cast 575. The surfactant/water and CNF/water weight ratios for all dispersion specimens were 1.71% and 1.14%, respectively. These proportions are the same as those used to make CNF-reinforced cement paste specimens for SEM imaging. Each sample for optical microscopy was prepared by placing a small drop of dispersion on a glass slide and covering it with a thin slip. A Zeiss Axiophot microscope was used in the transmitted mode with a 40 $\times$ dry objectives lens. For cryo-TEM, 5 μL of diluted dispersion was added onto perforated carbon grids (2 μm holes). Specimens were then plunge-frozen in liquid ethane at 100% relative humidity and transferred to a cryo-specimen holder that was maintained at -175 degrees Celsius (-283°F) throughout the length of the experiment. Observation was performed by an FEI Tecnai F20 transmission electron microscope.

Three CNF-reinforced hardened cement paste specimens were prepared for SEM observation. One of them contained VGCF-H CNFs and the other two contained Pyrograph CNFs. The mixture proportions of the specimens are shown in Table 2. In all specimens, the w/c was 0.35 and CNF/c and surfactant/c weight ratios were 0.4% and 0.6% respectively. Ordinary Type I portland cement was used. Due to compatibility issues that will be discussed later, only the superplasticizer was used as surfactant. For specimens 1 and 2, the CNFs were sonicated and dispersed in the solution of water and superplasticizer for 15 minutes and then the dispersion was added to and mixed with cement. For specimen 3, water-superplasticizer solution was added to a dry mix of cement and CNFs. A small multi-speed planetary mixer was used for mixing paste with a method similar to that of ASTM C 305-06, but with a longer mixing time (total of 7 minutes) to enhance paste uniformity. For each batch after the mixing was completed, the paste was cast into small beam molds. All of the beams were demolded after 24 hours and

then cured in lime saturated water. Three weeks after casting, the beams were broken, coated with 4 nm-thick Platinum/Palladium (80/20) layer to enhance surface conductivity while their fractured surfaces were observed by SEM. For SEM observation, the specimen made with VGCF-H was imaged by an FEI Quanta Q600FEG and the other specimens were imaged by a JEOL JSM-7500F.

Observations and discussion

The effect of surfactants on the dispersion of CNFs in water is illustrated in Fig. 3. Figure 3(a) shows VGCF-H fibers in water-Pluronic F98 solution after 15 minutes of sonication. They are well-dispersed and hardly any agglomeration can be seen. Fig. 3(b), on the other hand, shows a specimen made in the same condition but without any surfactant. The solution contains large clumps with only a small portion of CNFs floating individually in water. Figure 4 shows two types of poor dispersion of the CNFs in water. The first specimen (Fig. 4(a)) has the same composition as the one shown in Fig. 3(a), but it was only sonicated only for seconds. Clumps of entangled fibers can be seen; the sonication period has not been long enough to disentangle them. A similar pattern of agglomerations could be observed when insufficient amount of surfactant was used, even when the dispersion was sonicated for 15 minutes. Figure 4(b) shows a different type of agglomeration; the CNFs are bundled longitudinally. This type of texture forms when the dispersion is drying due to evaporation or absorption of water by a dry media such as a piece of cloth. Figure 5(a) shows VGCF-Hs in water-superplasticizer solution after 15 minutes of sonication; the image shows that the superplasticizer is not as effective as Pluronic F98 in dispersing this type of CNF. The distribution of CNFs in a location on the fractured surface of hardened cement paste made with this dispersion is shown in Fig. 5(b). The fibers are mostly separated, however this image does not represent the whole area of the fractured surface; in many locations no or little fibers could be seen. This suggests that a relatively uniform dispersion of CNFs in water does not guarantee a good dispersion in cement paste.

The effect of ultrasonic processing on the dispersion of CNFs is illustrated in Fig. 6; these are the optical microscopy images of the dispersion of Pyrograph in water-superplasticizer solution. Figure 6(a) shows the poor dispersion of CNFs in a superplasticizer-water solution that has been only hand-shaken for 7 minutes (the period of time used for mixing the cement paste specimens). In the sonicated mixture (Fig. 6(b)), fibers seem to be well-dispersed. It should be mentioned that these fibers were more dispersible than VGCF-H and their distribution quality in water was almost the same with both Pluronic F98 and superplasticizer. However, some small and mostly round dark areas can be seen (Fig. 6(b)). The dispersion was imaged by cryo-TEM in order to investigate the dark areas. Figure 7(a) shows a thread-like object which is curled and packed. Such curled threads formed more than half of the dark areas in the dispersion. The nature of these objects is still unknown, but they may be impurities. Figure 7(b) shows a bundle of smaller CNFs that has not been disentangled despite sonication. These bundles formed the rest of dark areas in the dispersion. Figure 8 shows the SEM image of one of such bundles in the cement paste made with the CNT dispersion (specimen 3). TEM observations, however, showed that the CNFs were well dispersed in the solution and the portion of bundled fibers and impurities was small. The other fact revealed by the TEM images is that many of the CNFs in the dispersion were shorter than the minimum length specified by the manufacturer (Fig. 9). The reason is probably, as also pointed out by Ozkan et al. (2008) who investigated the mechanical properties of a similar type of CNF, that some of the fibers break during sonication.

The SEM study of the fractured surface of hardened cement paste made from the CNFs, either from their dispersion in water-superplasticizer solution or dry mix with cement, showed that these fibers did not have an overall uniform distribution in cement paste. During the paste surface scanning via SEM, many areas were observed that were not covered with CNFs. The SEM images related to Pyrograph (specimen 3) also revealed the presence of several agglomerations, although the CNFs were dispersed well in the solution prior to making the cement paste. One such agglomeration is shown in Fig. 10. The underlying causes of reagglomeration of CNFs after adding the dispersion to cement can be explained through the effect of drying on dispersion. As mentioned earlier, initiation of drying of a CNF/T dispersion, and in general reduction in water/fiber ratio, results in bundling. When the dispersion is added to cement, the relatively large amount of cement adsorb the water rapidly. At this point the paste is still workable and fibers can move toward each other and form bundles.

As mentioned earlier, Fig. 10 shows a clump of CNFs within a pore in the hardened cement paste. These fibers are not covered by C-S-H or any hydration product, and they are not exposed by pull-out of the fibers during fracture. This is an indication of poor interfacial bond between the CNFs and matrix in several areas of the material with such cavities. In a CNT/F-reinforced composite the fibers are expected to be fully covered by and bonded to the matrix; otherwise, their presence is hardly beneficial. Bundling can limit the presence of hydration products in between the entangled fibers. This problem particularly exists in cementitious materials where the matrix

components are large relative to the CNT/F size and the space between them. Kim et al. (2006) have shown that even polymeric composites resins do not infiltrate into agglomerates of CNTs. However they, and later Li et al. (2008), solved this problem by different methods of CNT surface modification including acid treatment. **Figure 11** reveals another issue regarding CNF-cement matrix interfacial bond; this figure shows two different scenarios of what can happen to CNFs that bridge a crack. The image in **Fig. 11(a)** is taken from the fractured surface of specimen 2 (in which CNFs were not sonicated in water). Several occurrences of fiber pullout are shown. The image in **Fig. 11(b)** is taken from specimen 3 (in which CNFs were first sonicated in water-superplasticizer solution). In this image, two CNFs can be seen that are fractured at the same level as crack surface. This shows that the fibers did not get pulled out and the bond between the fibers and matrix was so strong that the CNTs broke when the crack propagated through them. The observations in **Fig. 11** indicate that it is possible to control the interfacial bond strength between CNFs and cementitious matrix, and this strength can be high enough to prevent pull-out. Additionally, although the occurrence of fiber pull-out and fracture was seen both in specimens 2 and 3, it is possible that sonication, due to the roughening of fiber surface, can improve the bond. More investigation is required to prove this hypothesis.

As the experimental results showed, Pluronic F98 is more effective (compared to polycarboxylate-based superplasticizers) in disagglomeration of the CNFs in water. Stronger surfactants may prevent rebundling of the fibers during and after paste mixing. However, many of the effective surfactants are incompatible with cement hydration. For example, the experiments of the authors have shown that the addition of Pluronic F98 to cement paste increases the amount of entrapped air remarkably. Using Sodium Dodecylbenzene Sulfonate, which is an effective anionic surfactant, the cement paste entrapped air about five times more than is typical in plain cement paste. The paste also did not reach initial set until after 24 hours. Gum Arabic is a natural polymer that has shown to be an effective surfactant for dispersing CNTs in aqueous media (Bandyopadhyaya et al. 2002). However, it was observed by the authors that when some polycarboxylate-based superplasticizer was added to a dispersion produced by sonicating 1.0% weight of CNTs in a Gum Arabic-water solution (2.0% weight), the fibers reagglomerated and the dispersion turned into a gel-like material. There are stable CNT aqueous dispersions available in the market, like AquaCyl produced by Nanocyl Company, but they have some negatives effects on cement hydration. Cwirzen et al. (2008) found that Gum Arabic slowed down the hydration reactions and decreased the compressive strength of hardened cement paste. All these findings show that a hydration-compatible surfactant may not always be the solution to the problem of producing cementitious composites with uniformly distributed and well-bonded CNT/Fs, and approaches such as surface functionalization and implantation on cement grains should be further investigated.

CONCLUDING REMARKS

A summary of the past investigations on the reinforcement of cementitious composites with CNTs was presented. Issues on dispersion, fiber-matrix interfacial bond, and surface functionalization were discussed. Studies focused on incorporating CNFs in cementitious composites are scarce. CNFs have much lower surface area compared to CNTs and are easier to disperse. An experimental program on two types of CNFs was presented. It was found that a polycarboxylate-based superplasticizer could properly disperse a relatively high concentration (more than 1.0%) of one type of the fibers in water. However, the SEM images of hardened cement paste revealed the presence of bundles, clumps, and distribution non-uniformities. This suggests that some of the fibers reagglomerate during and after paste mixing. Reagglomeration can be due to the adsorption of water by cement from dispersion. The SEM observations proved the possibility of the occurrence of both CNF pull-out and fracture, and therefore the controllability of CNF-cement matrix interfacial bond. The SEM images also showed that many of the agglomerated CNFs were not covered with or bonded to the matrix, since the paste had not infiltrated through them; this indicates the importance of examining additional approaches (such as fiber surface functionalization) to optimize both bond and dispersion. Seeking additional approaches to ensure dispersion and bond than surfactants is also important since more effective surfactants can negatively affect cement hydration. Moreover, more dispersible CNFs require less sonication, which would be another advantage since long period of sonication can break and shorten the fibers.

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Table 1—The CNFs used in the experiment and the imaging methods used to study their dispersion

Fiber name	Producer	Average diameter, nm	Average length, μm	Specific surface area, m^2/g	Optical microscopy	TEM	SEM
VGCF-H	Showa Denko, Japan.	150	10-20	13	Yes	No	Yes
Pyrograph PR-24 (PS)	Applied Science, Ohio.	60-150	30-100	50-60	Yes	Yes	Yes

Note: $1 \text{ m}^2/\text{g} = 4882 \text{ ft}^2/\text{lb}$.

Table 2—Mixture proportions of the cement paste specimens

Batch No.	w/c	VGCF-H/c	Pyrograph/c, %	Superplastiszer/c, %	Sonication
1	0.35	0.4	0	0.6	Yes
2	0.35	0	0.4	0.6	No
3	0.35	0	0.4	0.6	Yes

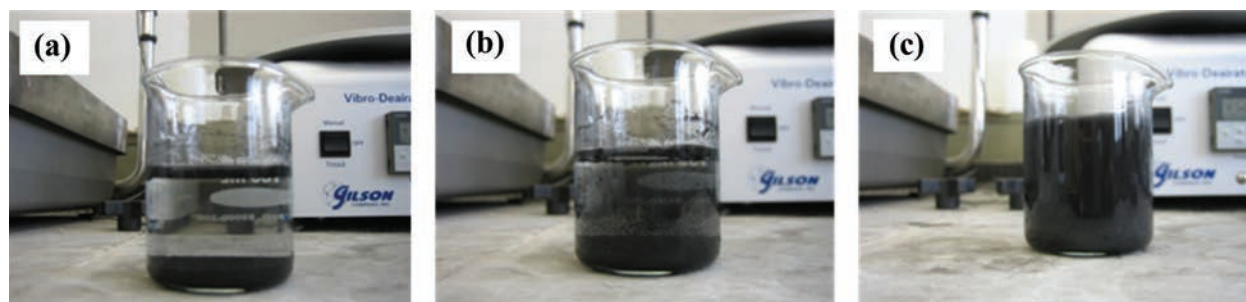


Fig. 1—Effect of CNF dispersion quality on the transparency of solutions. All three specimens have the same CNF/water ratio. (a) CNFs were added to only water and mixed by a hand stirrer, which resulted in poor dispersion and as a result high transparency; (b) CNFs were added to a solution of water and surfactant and mixed by a hand stirrer; this resulted in a slightly better and darker dispersion; and (c) CNFs were sonicated in a water-surfactant solution. This produced a good and very dark dispersion.

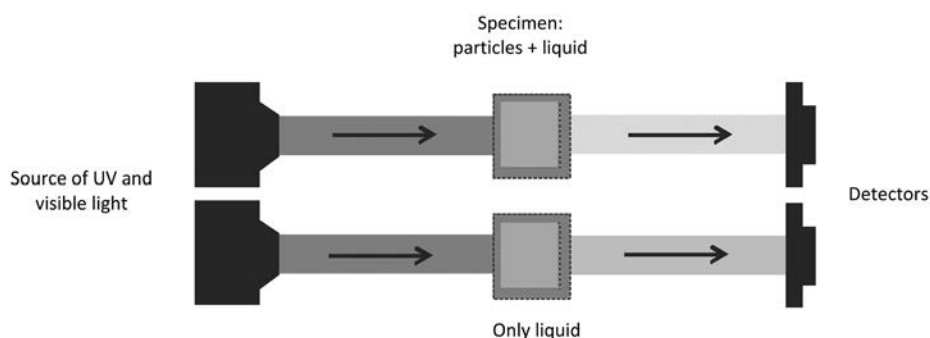


Fig. 2—Schematic layout of a UV-vis spectroscopy device, used for quantifying the dispersion of particles in a transparent medium. From the portion of radiation received by the detectors, the absorption capacity of the particles, and thus the uniformity of their distribution, can be determined.

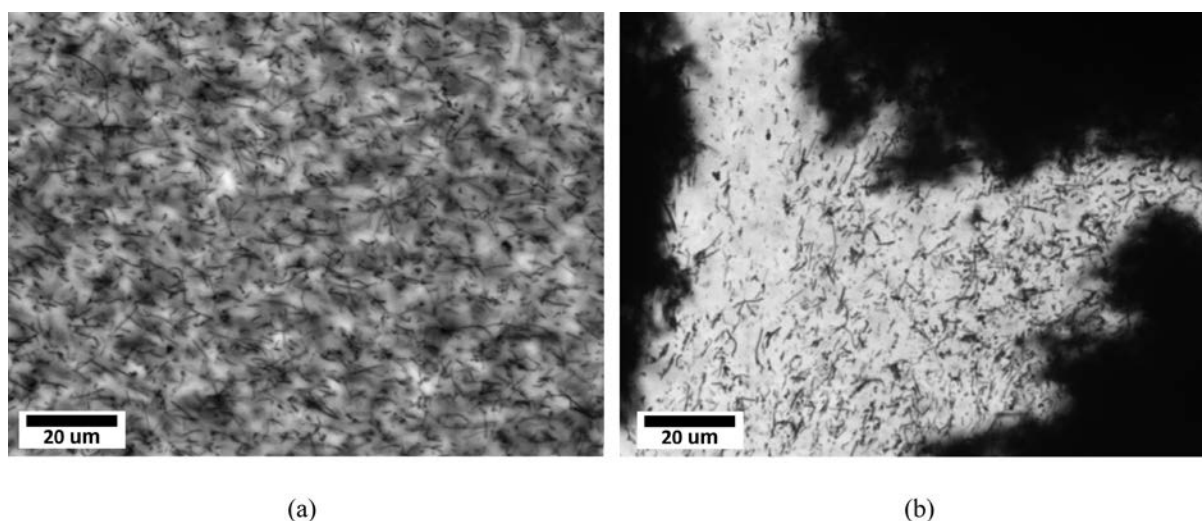


Fig. 3—Effect of surfactants on the dispersion of CNFs: optical microscopy image of the distribution of VGCF-Hs: (a) in water-Pluronic F98 solution; and (b) only in water. Both specimens were sonicated for 15 minutes.

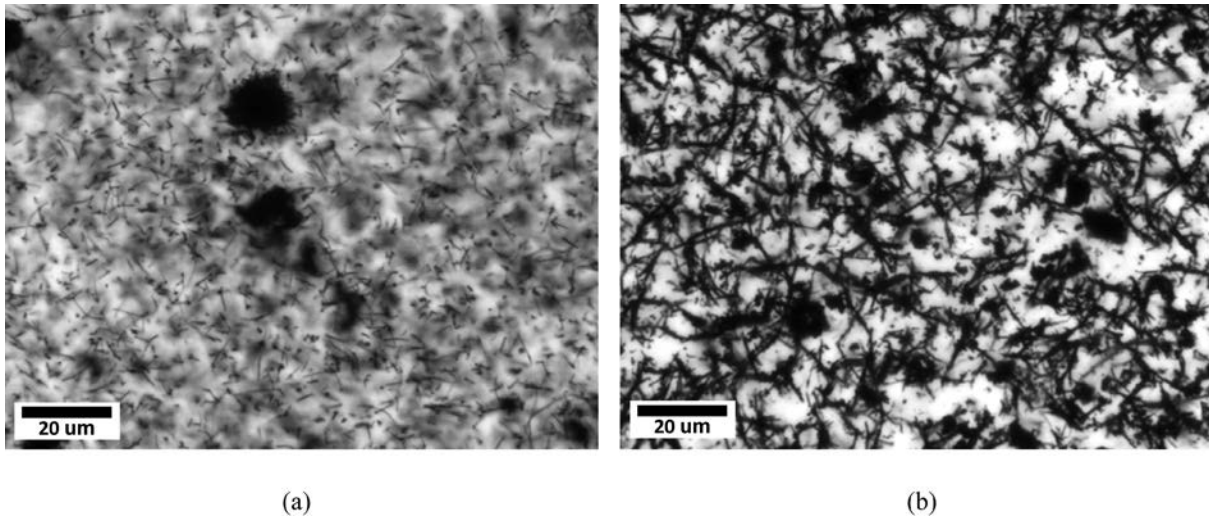


Fig. 4—Two types of poor dispersion of CNFs (VGCF-Hs) in water: (a) nondisentangled clumps of CNF due to insufficient sonication; and (b) rebundling of CNFs as a result of drying. Both specimens have the same composition with Pluronic F98 was used as surfactant.

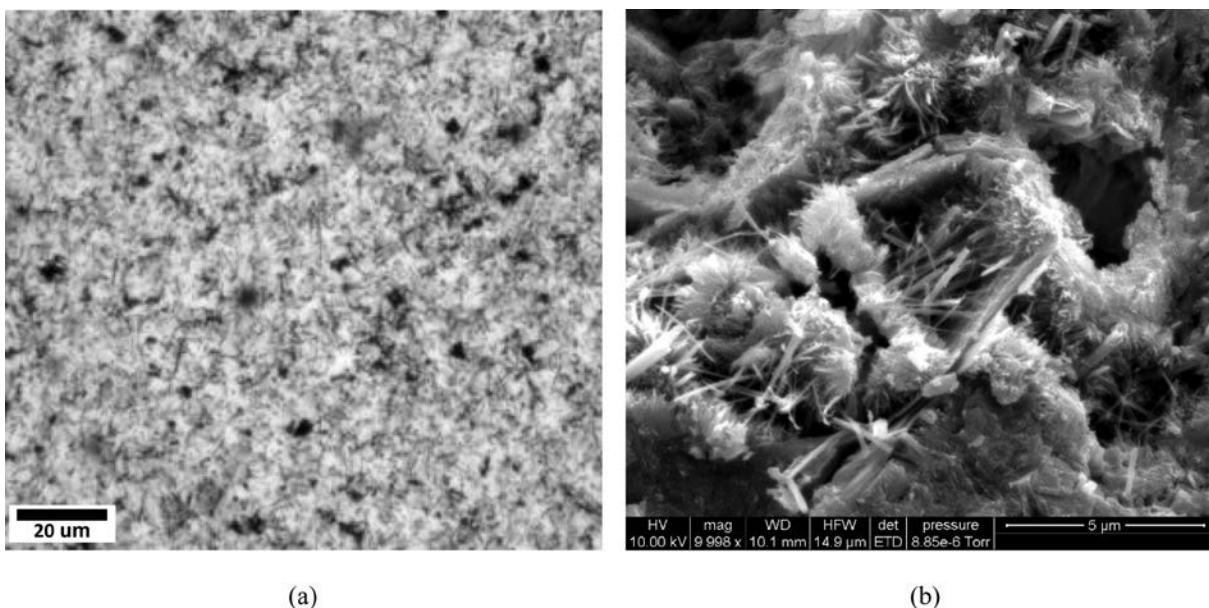


Fig. 5—Comparison between the distribution of CNFs in water and cement paste. (a) Optical micrograph of the dispersion of VGCF-Hs in water-superplasticizer solution. The distribution is relatively uniform, but some of the smaller fibers are agglomerated; and (b) SEM image of the hardened cement paste in a location with a relatively high concentration of CNFs. The paste was made with the dispersion in (a). The majority of larger fibers are separated. However, this image does not represent the distribution of CNFs in the matrix. In several areas of the fractured surface, no or few fibers could be observed by SEM.

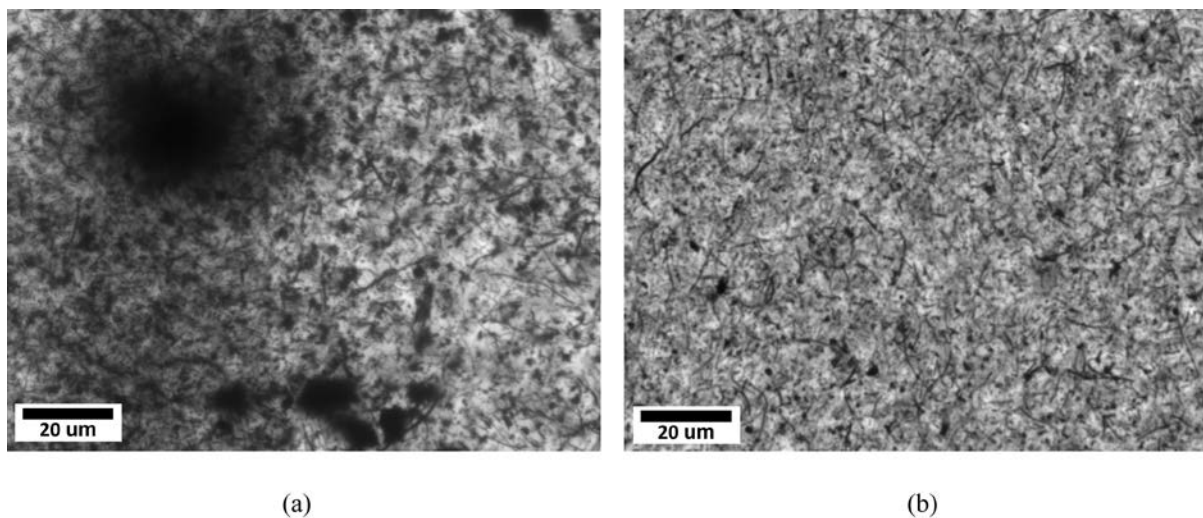


Fig. 6—Effect of sonication on the dispersion of Pyrograph CNFs in aqueous media. In both specimens, the proportions are the same and the fibers have been added to a water-superplasticizer solution. (a) Only hand-shaken; and (b) sonicated for 15 minutes.

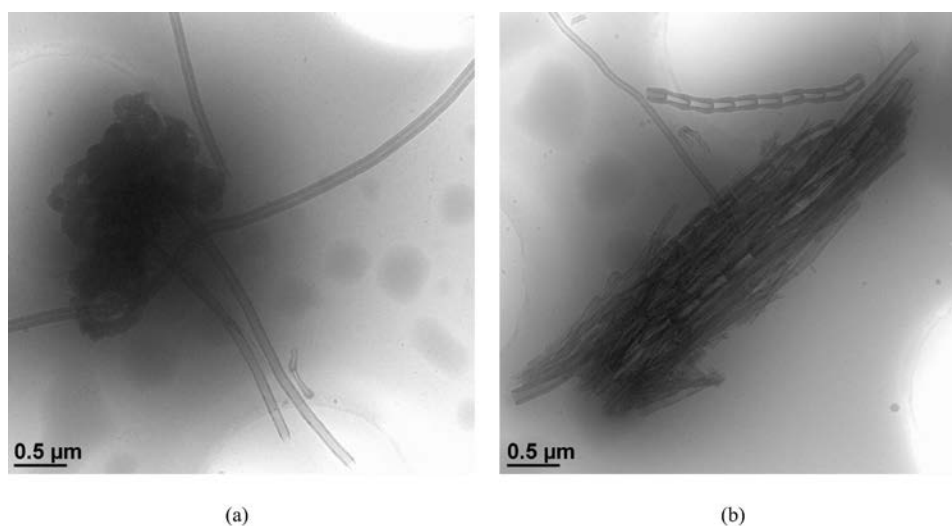


Fig. 7—Cryo-TEM images of some undesired features in the sonicated dispersion of Pyrograph shown in Fig. 10(a). (a) Impurity in the shape of a curled thread; and (b) longitudinal bundle of CNFs caused by parallel agglomeration of the fibers.

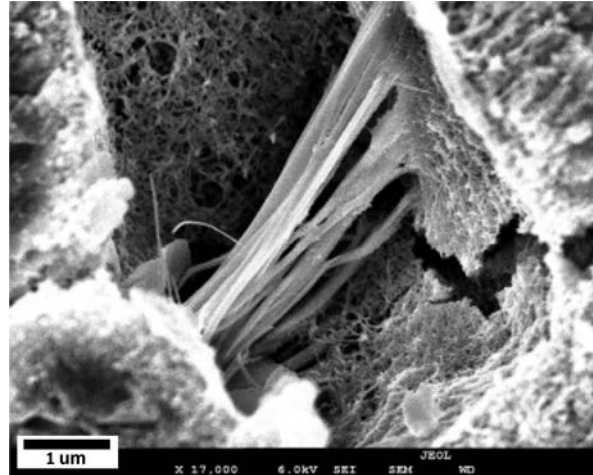


Fig. 8—SEM image of a longitudinal bundle of Pyrograph CNFs in hardened cement paste. The bundle is very similar to those observed in the dispersion used to make the paste (Fig. 7(b)). The image also shows that the fibers are not covered by hydration products.

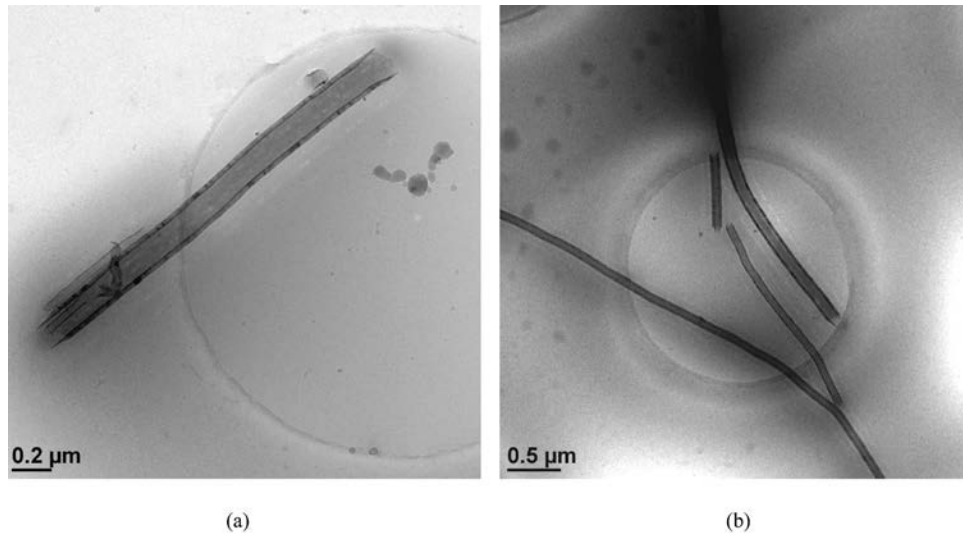


Fig. 9—Cryo-TEM images of Pyrograph showing different diameters and lengths of the CNFs. These fibers have been sonicated in an aqueous solution for 15 minutes and their aspect ratios are noticeably smaller than those of non-sonicated fibers. This means that long period of ultrasonic processing can break and shorten many of the CNFs.