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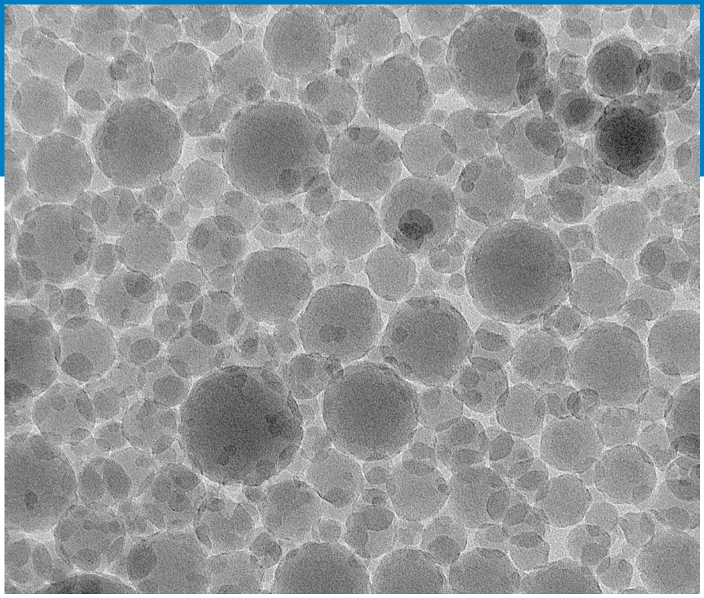

Nanotechnology for Improved Concrete Performance

Editors:
Mahmoud Reda Taha and Mohamed T. Bassuoni

SP-335

American Concrete Institute
Always advancing

Nanotechnology for Improved Concrete Performance

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The papers in this volume have been reviewed under Institute publication procedures by individuals expert in the subject areas of the papers.

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PREFACE

Nanotechnology for Improved Concrete Performance

Preface: Many of the papers presented in this volume were included in the two-part session *Nanotechnology for Improved Concrete Performance*, sponsored by ACI Committee 241, Nanotechnology of Concrete at the ACI Convention in Philadelphia, PA, on October 26, 2016. In line with the practice and requirements of the American Concrete Institute, peer review, followed by appropriate response and revision by authors, has been implemented.

In the last decade, there have been considerable research efforts aimed at improving the mechanical and durability performance of concrete using nanotechnology. Exemplar work includes using nanoparticles to improve the hydration process of cement, incorporating nanomaterials to alter the mechanical and durability characteristics of concrete, and providing a new source for the self-sensing functionality of concrete. The scope of these papers encompasses experimental and applied research examining the use of nanomaterials to improve the performance of concrete at large. Readers are urged to critically evaluate the work presented herein, in light of the substantial body of knowledge and scientific literature on this topic.

We dedicate this volume of papers to the memory of Professor Robert (Bob) L. Day (1950-2014), of The University of Calgary, Canada and past Chairman of Canadian Standards Association (CSA) Committee A23.1/A23.2 (Concrete Materials and Construction), for his invaluable contributions to the field of concrete science and his remarkable mentoring of numerous concrete professionals worldwide.

The editors sincerely thank all the presenters in the 2016 session and the authors of the articles included in this special publication, as well as the reviewers for their thorough and objective assessment of the papers. Their technical contributions provide a holistic perspective of *Nanotechnology for Improved Concrete Performance*.

Mahmoud Reda Taha, Editor
Mohamed T. Bassuoni, Co-editor

TABLE OF CONTENTS

MULTI-SCALE FIBER REINFORCEMENT FOR CRACKING RESISTANCE IN CEMENT MORTARS

Joshua Hogancamp, Cesario Tavares, and Zachary Grasley

SYNOPSIS:

The current state of the art in fiber-reinforced cement-based materials indicates that adding multiple fiber types or sizes primarily creates a superpositioned behavior state: the behavior from each fiber type separately is added to the composite behavior of the material. Carbon nanofibers (CNFs) and milled carbon microfibers (MCMFs) can increase cracking resistance in cement-based materials by bridging cracks, although CNFs bridge cracks significantly smaller than cracks bridged by MCMFs. This research suggests that multi-scale fiber reinforcement (CNFs with MCMFs) might add compounded benefits to cracking resistance. Tests evaluating cracking resistance were performed utilizing a restrained-ring drying shrinkage test with Portland cement mortars. The CNFs and/or MCMFs were pre-mixed with cement using a sonication/distillation technique and/or rotary tumbling. Concentrations of CNFs and MCMFs were tested up to 5% and 6% by mass of cement, respectively. Restrained ring tests on mortar with high concentrations of CNFs or MCMFs reveal delayed cracking time by factors up to 6.4 or 2.6, respectively. Combining CNFs with MCMFs delayed cracking by a factor of at least 52. The increase in cracking resistance is attributed to the combined effects of bridging cracks of multiple sizes.

Keywords: Carbon nanofiber; carbon microfiber; mortar; cracking resistance

BIOGRAPHIES

Dr. Joshua Hogancamp graduated from Texas A&M University in 2017 with a focus in using microfine cementitious materials to enhance the efficacy of carbon nanofibers in mortars. He is currently a Post-Doctoral Appointee at Sandia National Laboratories in Albuquerque, NM.

Cesario Tavares graduated in 2014 with a Civil Engineering Master's Degree, with focus on Materials and Construction Processes, at Faculty of Engineering of University of Porto, Portugal. After three years in the construction industry as an Assistant Site Manager, he is currently a PhD candidate and Graduate Research Assistant in Texas A&M University.

Dr. Zachary Grasley received his PhD at University of Illinois at Urbana-Champaign in 2006. He is a professor, Presidential Impact Fellow, and Director of the Center for Infrastructure Renewal at Texas A&M University.

INTRODUCTION

Portland cement-based materials (PCBMs) are known for exhibiting a brittle behavior under load, with a strong resistance to compression contrasting a weak response under tension, and a tendency to crack during all ages of the material. Plastic shrinkage cracking occurs during and immediately after the initial set (period in which the matrix begins to harden); drying shrinkage cracking often occurs in the early life although it can occur at any age; load-induced cracking can occur at any age despite occurring more often during initial loading; fatigue cracking can occur after a significant period of time in the composite life; and degradation such as freeze-thaw, sulfate attack, or alkali-silica reaction can also generate cracks (1). Fibers reinforcing concrete and mortar have the ability to bridge and restrain cracks after they form, increasing ductility of the composite material and enabling it to retain some tensile capacity after cracking (2-5). The most common fiber types used in industry are macrofibers such as steel and synthetic or microfibers such as carbon or synthetic (6-8). The advent of mass-produced carbon nanofibers (CNFs) and carbon nanotubes (CNTs) has led to significant advances in nano-reinforced PCBMs including increases in flexural strength, compressive strength, plastic shrinkage cracking resistance, and Young's modulus (9-17).

The current state of the art in CNF and CNT fiber-reinforced concretes and mortars (FRCs) suggests that adding multiple fiber types or sizes results in a superpositioned behavior state, that is, the behavior from each fiber type separately is added to the composite behavior of the PCBM (18). However, research has yet resulted in a significant advance in creating compounded benefits from multiple fiber types or sizes. The objective of this research is to elucidate that using multi-scale fiber reinforcement in PCBMs can add compounded benefits to restrained ring drying cracking resistance that are greater than the sum of the benefits from either fiber alone.

THEORY

Microfibers and macrofibers are typically used in industry to bridge cracks after crack formation, and the fibers add little benefit prior to cracking. The fibers require a certain level of strain in the composite material before they become 'active' in brittle materials such as PCBMs. However, recent studies(19, 20) prove that high concentrations of CNFs in a microfine cement matrix can delay drying shrinkage cracking in restrained ring tests by bridging nearly undetectable microcracks and preventing the formation of a macrocrack. The plethora of microcracks bridged by CNFs create an 'apparent strain' as demonstrated in Figure 1. The cement paste experiences a mechanical elastic strain from the applied load, and the formation of multiple microcracks bridged by CNFs creates an additional apparent strain.

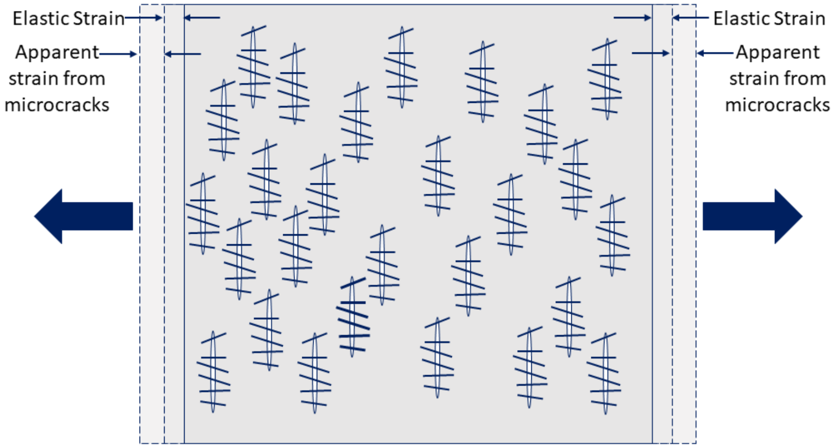

Figure 1—Sechematic of mechanical elastic strain and apparent strain from an applied load on cement paste with CNFs bridging across nearly undetectable microcracks.

The combined matrix elastic strain and bridged microcrack apparent strain could together be a significant total strain to 'activate' microfibers before the formation of a macrocrack. Another type of fibers chosen for this study are MCMFs, which are some of the smallest microfibers available both in length and diameter, and can be blended with cement in high concentrations with little to no clumping during mixing as shown in Figure 2.

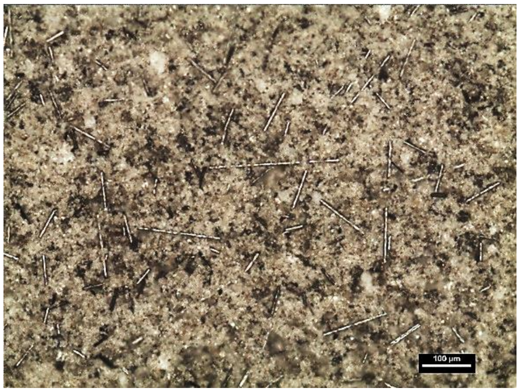

Figure 2—Unhydrated ordinary Portland cement (OPC) with 4wt% MCMFs. The MCMFs are seen as white lines in this image. The size scale in the bottom-right corner is 100 μm ($3.9*10^{-3}$ in).

The primary purpose of this research is to introduce the concept of using high concentrations of CNFs combined with MCMFs to increase cracking resistance, presumably by bridging crack sizes across multiple orders of magnitude. To the authors' knowledge, cracking resistance improvements on the scale present here using only fiber additions and without the formation of a macrocrack have not been seen before in PCBMs. These cracking resistance improvements require both CNFs and MCMFs. Optimum mixture combinations lie beyond the scope of this document.

MATERIALS, METHODS, AND EXPERIMENTAL DETAILS

Table 1 lists the types and properties of the CNFs and milled carbon microfibers (MCMFs) used in this research.

Table 1—Fiber properties.

Fiber	Diameter	Length	Tensile Strength	Young's Modulus
CNF	~100 nm ($3.94*10^{-6}$ in)	50 – 200 μm ($2.0 – 7.9*10^{-3}$ in)	2920 MPa (423 ksi)	240 GPa (34800 ksi)
MCMF	7.2 μm ($0.28*10^{-3}$ in)	~100 μm[1] ($\sim 3.9*10^{-3}$ in)	4137 MPa (600 ksi)	242 GPa (35100 ksi)
[1]Length varies due to ball-milling process.				

High concentrations of CNFs (greater than ~0.5wt%) must be pre-mixed with a microfine cement using a sonication/alcohol distillation technique(19), and the MCMFs can be added to the sonication/alcohol distillation process (patent: CARBON Cement(21)). A microfine cement is required in lieu of OPC for high concentrations of CNFs (above ~0.3wt% CNFs) to prevent geometric clustering of fibers(22) and allow higher concentrations. This mixing procedure provides an excellent dispersion of both CNFs and MCMFs in the cement at very high concentrations with no fiber clumping/bundling/balling during mixing. A probe-tipped sonicator at 40% amplitude and 20 kHz sonicated the mixture while using a magnetic stirring plate to keep all solids in suspension. The mixing process for mortar with CNFs is:

1. The CNFs are sonicated in 100% pure ethyl alcohol.
2. Cement and MCMFs are added to the CNF/alcohol mixture in correct proportions to obtain the desired concentration of fibers and cement.
3. The alcohol/cement/fiber slurry is sonicated further with constant mechanical stirring.
4. After sonication, the slurry is distilled in a distillation column to remove and recapture the alcohol, leaving behind a pre-mixed cement/fiber powder.
5. The pre-mixed cement/fiber powder is oven-dried in a well-ventilated oven for 24 hours to ensure removal of all alcohol.

Cement mixtures with ordinary Type I/II Portland cement (OPC) and MCMFs did not require the alcohol sonication/distillation technique. The MCMFs were dry-mixed with the cement in a rotary tumbler in appropriate concentrations, and the pre-mixed cement/MCMF mixture could then be used to make mortar with no fiber clumping issues. Note that, with CNFs and/or MCMFs, the fibers must be mixed with the cement prior to use in mortar or concrete; however, the fiber/cement dry mixture can be directly added with aggregates and water in ready-mix applications.

Restrained ring drying shrinkage tests are often used to assess the cracking tendency of partially restrained concrete(23-26). A restrained ring drying shrinkage test developed for use with mortars(20) was utilized to determine the efficacy of the CNFs and/or MCMFs at preventing cracking as shown in Figure 3. In the restrained ring drying shrinkage test (or simply the "restrained ring test"), a thick ring of mortar is poured around short thin-walled steel cylinder fitted with strain gages on the internal radial surface. Mortar rings were allowed to cure sealed for 24 ± 0.5 hours at 23°C (73.4°F). The rings were then demolded, the tops of the mortar were sealed with adhesive-backed aluminum foil to prevent moisture loss, and the relative humidity (RH) was reduced to 50% to initiate drying on the outer radial surface of the mortar ring. The rings were kept in an environmental control system to ensure accurate temperature and humidity control during testing. The strain in the steel ring was recorded at 5-minute intervals. The restrained ring test is optimal for this research since any formation of a macrocrack is observed as a sudden drop in strain in the inner steel ring. The initiation of microcracking is observed in this test as a sudden change in slope of strain vs drying time with no reduction in strain(20).

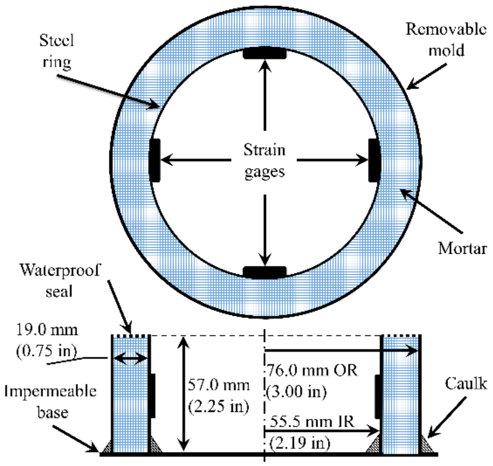

Figure 3—Ring test setup. "IR" and "OR" represent inner radius and outer radius, respectively. A non-stick sheet is placed between the mortar and the impermeable base.(20)

The mixture nomenclature used in this research is defined as

‘Cement type’ ‘w/c ratio’ – ‘wt% CNFs’ . ‘wt% MCMFs’

For example, F0.5-2.2 is a microfine cement mortar with a w/c ratio of 0.5, 2wt% CNFs, and 2wt% MCMFs. OPC0.4-0.2 is an OPC mortar with a w/c ratio of 0.4, no CNFs, and 2wt% MCMFs.

Conversions between concentrations of fibers by mass of cement (wt%) and by volume of cement (vol%) are shown in Table 2, and mixture details performed in this research are shown in Table 3. All mortar mixtures consisted of cement (either microfine or Type I/II), ASTM 20-30 uniformly graded silica sand with a 1.75 sand-to-cement ratio by mass, and water. The Blaine fineness of the OPC and microfine cements are 350 m^2/kg (1710 ft^2/lb) and >12,000 m^2/kg (58,600 ft^2/lb), respectively. The OPC cement particle size ranges from 1 – 100 µm ($4*10^{-5}$ – $4*10^{-3}$ in) while the microfine cement is almost uniformly graded at 0.1 µm ($4*10^{-6}$ in). Gradations of each cement type were measured using x-ray fluorescence. Microfine cement mixtures required polycarboxylate high-range water reducing admixture and 3% by mass of cement sucrose-based set retarders; OPC mixtures required neither. Mixture flowability was designed to allow placement of the material into forms without forming voids, segregation, or bleeding. A minimum of two identical tests were performed per mixture. Further testing was not required for proof of concept due to the excellent agreement between the duplicate tests(20).

Table 2—Conversion between concentrations by mass of cement (wt%) and by volume of cement (vol%). Conversions apply to both carbon fiber types used in this document.

Wt% Concentration	Vol% Concentration	Concentration of Fibers by Volume of Mortar (%)	
		W/C Ratio 0.4	W/C Ratio 0.5
1	1.97	0.45	0.42
2	3.94	0.89	0.83
3	5.91	1.33	1.24
4	7.88	1.76	1.65
5	9.85	2.19	2.05
6	11.82	2.62	2.45